— SECTION B —

CHEMICAL SCIENCES

Contents

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THE CONCENTRATED SOLUTION VISCOSITY OF GR-S: ITS VARIATION (IN BENZENE) WITH TEMPERATURE AND CONCENTRATION[1]

By L. H. CRAGG, L. M. FAICHNEY[2], AND H. F. OLDS[3]

Abstract

With a falling ball viscometer, measurements of the viscosity of solutions of GR-S in benzene have been made at very low rates of shear, at concentrations ranging from 10 to 19%, and at temperatures ranging from 10° to 35° C. Within these limits, the viscosity of a solution of GR-S in benzene is given by the equation

$$\eta \text{ (poises)} = 4.53 \times 10^{-4} \exp\left\{\left(0.815 + \frac{656}{T}\right) C_w^{\frac{1}{3}}\right\}.$$ Extrapolation, by means

of this equation, to 100% polymer yields a value of 13.0 kcal. per mole for the energy of activation of flow of GR-S; this value, though of dubious antecedence, is yet of interest because it approximates that expected for GR-S on the basis of the behavior of such polymers as natural rubber and polystyrene.

Introduction

Measurements of the viscosity of solutions of high-polymeric substances, both natural and synthetic, have long been put to practical uses in industry. More recently the viscosity behavior of such substances in very dilute solution has been successfully related to the molecular size of the polymer. When the molecules could be assumed to be essentially linear, the intrinsic viscosity (6) has been related empirically and, recently, theoretically (7, 8) to the average molecular weight of the polymeric substance. It seems evident, however, that the viscosity behavior in concentrated solution, where the polymer molecules come more frequently and more intimately in contact with each other, would be more likely to be governed by the structure and configuration of the molecules. Specifically, concentrated solution viscosity might be expected to give a better indication of branching than dilute solution viscosity (4). It was with this hope that, some time ago, we undertook the investigation of the rheological behavior of concentrated solutions of the synthetic rubber GR-S.

It is well known that concentrated solutions of such natural high polymers as cellulose and rubber are non-Newtonian liquids, their 'viscosity' varying with the rate of shear. Strictly, therefore, these solutions cannot be said to

have a viscosity at a given temperature, and the flow behavior can be properly characterized only by determining the 'apparent viscosity' (5, p. 280) at different rates of shear. For this purpose the most suitable instrument is a rotational viscometer (5) (particularly if thixotropic behavior is also to be studied), and such an instrument has been adopted for most of our work. Although it is possible with this type of instrument to determine the effect on the apparent viscosity of changes in temperature and concentration, these effects may be much more conveniently and rapidly measured with a falling-ball viscometer (5) (an apparatus that has the additional advantage of being simple, relatively inexpensive, and readily available). Since such information was necessary to our work, a falling-ball viscometer was constructed and measurements were made.

Experiments

Two entirely independent series of measurements were made (L.M.F. and H.F.O.) with different samples of polymer, over slightly different ranges of temperature and concentration, and with minor differences in technique. The results obtained were in good agreement.

Apparatus*

The viscometer was patterned on the one used by Oppen and Schuette (20) and is shown diagrammatically in Fig. 1. Three interchangeable *fall tubes*, of dimensions shown in Fig. 1 and Table I, were constructed of Pyrex tubing; to avoid parallax the lines were scratched completely around the tube. The dimensions are such that the falling ball reaches thermal equilibrium and constant velocity before it passes C. The *centering tube* was flared at the bottom to minimize the tendency for the falling ball to be pulled to one side on leaving the opening at B; it was also provided with a removable inner tube (as shown) for use with balls of very small diameter (viz. 1/32 and 3/64 in. diam.).

To provide the close *temperature control* required, the viscometer tube was immersed, to a level above A, in water whose temperature at any one position in the bath was controlled to ±0.02° C. by means of a deKhotinsky bimetallic regulator operating through a sensitive electronic relay. Although the water filled a rather large cylindrical vessel (2 ft. high by 1 ft. in diameter) stirring was so efficient that at 25.00° C. the extreme difference between temperature readings in various positions did not exceed 0.08° C. in the bath and 0.05° C. in the solution. Since the variation of viscosity with temperature (*vide infra*) is such that a difference of 0.1° C. would result in a difference in viscosity of only 0.3%—which in these experiments is much less than the experimental error—this degree of control is quite sufficient.

* For a full, and very helpful, discussion of the falling-ball viscometer and its use, see Barr (5, Chap. VIII).

The *balls* used in both series were manufactured by Miniature Precision Bearings, Keene, N.H., who guaranteed that the diameters of the balls of a given stated size did not vary by more than 0.0001 in. Diameters were
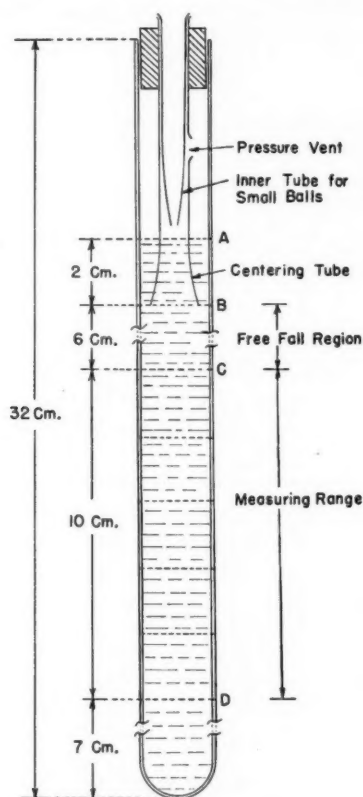
FIG. 1.   *The tube of the falling-ball viscometer and its dimensions.*

TABLE I

DIMENSIONS OF THE VISCOMETER TUBES

	1	2	3
Diameter, cm.	2.16	2.16	2.16
Measured fall, cm.	10.02	9.98	9.91

measured, and they agreed closely with the stated diameters. Balls were weighed in lots of 10, 20, 30, 40, and 50 and the average weight computed; these measurements indicated that the balls were indeed remarkably uniform.

Densities were then calculated on the assumption that the balls were spherical. The balls were of stainless steel and were kept under mineral oil when not in use.

The fall times were measured with a calibrated stopwatch reading to 1/10 sec.

Materials

The benzene used throughout was technical grade, obtained from the Steel Company of Canada, Hamilton, and redistilled before use.

The samples of synthetic rubber were normal plant GR–S obtained from Polymer Corporation Ltd., Sarnia, and used as received (i.e., without further treatment). The sample used in Series I was obtained October 27, 1945, that used in Series II (HFO) was from lot S-2503* obtained November 13, 1946.

Technique

Solutions of GR–S in benzene ranging in concentration from 10 to 19% by weight (gm. per 100 gm. solution) were investigated. These gave a wide range of viscosities; in solutions more dilute than 10% the ball fell too rapidly to permit precise timing, whereas in solutions more concentrated than 19% the rate of fall was so slow as to make measurements tedious.

Solutions were prepared by adding benzene to a weighed quantity of finely cut GR–S in a ground-glass-stoppered bottle, binding the stopper in place, and rotating the bottle about three times per minute till solution was complete. With a steel roller in the bottle and with coaxial rotation (Series I) this required from 6 to 15 hr., the actual time depending on the concentration; without the roller and with end over end rotation (Series II) the time required was 15 to 24 hr. The density, ρ, of the solutions was measured at the temperature of the experiment with a Westphal balance; to sufficient precision the density was independent of the concentration and varied with the temperature according to the expression

$$\rho_\theta = 0.880 + 0.001(25 - \theta),$$

where θ is the temperature in degrees Centigrade.

Viscosities of each solution were measured at 5° C. intervals in the range 15° to 35° C. (Series I) and 10° to 35° C. (Series II). (Above 35° C. bubbles appeared in the solution and interfered with the free fall of the balls.) For each run, the solution was placed in the fall tube to the desired height (A, Fig. 1) and left in the bath at the desired temperature till thermal equilibrium was established. In making measurements, care was taken to mount the fall tube vertically, to wash each ball in benzene and dry before use, and to allow sufficient time between successive falls for any thixotropic breakdown in the solution to be 'repaired'.†

* *See reference (21) for full description of this sample.*

† *No thixotropic effect was observed in solutions up to 12.5%. With more concentrated solutions a wait of 30 min. between falls was sufficient to ensure reproducibility of times of fall to 1%.*

Results

Viscosities determined in this way are recorded in graphical form in Figs. 2 and 3. All these values were calculated from data obtained with 1/16 in. balls (see discussion below); typical data are given in Tables II and III to illustrate the precision attained in multiplicate determinations of fall time in a given solution.

TABLE II

APPARENT VISCOSITIES OF SOLUTIONS OF GR–S IN BENZENE (FROM SERIES I)

Concentration, C_w, gm./100 gm. soln.	Temperature, $\theta°$ C.	Fall time, t sec.	Viscosity,* η_s poises
10.2	15.0	13.9 14.3 14.0	13.3
	20.0	12.5 12.5 12.6	11.9
	25.0	10.9 10.9 10.9	10.3
	30.0	10.0 9.9 9.9	9.4
	35.0	8.9 8.9 8.6	8.5
14.5$_8$	15.0	101.2 100.0 100.1	94.9
	20.0	86.4 86.7 87.1	81.6
	25.0	73.5 73.1 73.2	68.9
	30.0	62.7 62.8 62.6	59.1
	35.0	55.3 56.1 56.1	52.9
18.5$_3$	15.0	430.6 432.6 432.5	410
	20.0	373.7 371.5 372.3	353

* Calculated by the simple Stokes formula: $\eta = \frac{2}{9}(\sigma - \rho)gr^2/v$, where σ is the density of the ball, ρ the density of the solution, r the radius of the ball, v the terminal velocity of its fall; no correction for the wall effect has been made here.

TABLE II—*Concluded*

APPARENT VISCOSITIES OF SOLUTIONS OF GR–S IN BENZENE (FROM SERIES I)—*Concluded*

Concentration, C_w, gm./100 gm. soln.	Temperature, $\theta°$ C.	Fall time, t sec.	Viscosity,* η_a poises
	25.0	313.5 314.6 316.3	299
	30.0	266.8 267.3 267.7	254
	35.0	232.3 232.6 231.8	221

* *Calculated by the simple Stokes formula:* $\eta = \frac{2}{9}(\sigma - \rho)gr^2/v$, *where σ is the density of the ball, ρ the density of the solution, r the radius of the ball, v the terminal velocity of its fall; no correction for the wall effect has been made here.*

TABLE III

APPARENT VISCOSITIES OF SOLUTIONS OF GR–S IN BENZENE (FROM SERIES II) AT 25.00° C.

Concentration, C_w, gm./100 gm. soln.	Fall time, t sec.	Viscosity, η_a	
		Observed	Calculated
10.2_3	10.5 10.6 10.6	10.0	10.0
12.6_1	30.8 30.8 30.9	29.0	29.1
14.8_0	73.5 74.0 74.0	69.8	71.3
16.3_6	137.4 137.3 137.4	130	129.1
18.0_4	262.2 262.5 262.9	248	238
18.8_6	334.0 334.1 335.5	311	318

Discussion

Of the methods of expressing the relation between viscosity and temperature that might have been used, the empirical equation

$$\eta = Ae^{B/T} \tag{1}$$

or

$$\log \eta = A' + B'\left(\frac{1}{T}\right), \tag{2}$$

where T is the temperature in °K., has proved satisfactory in so many instances (9), both with pure liquids and with solutions, that it was given preference here. Again it proves its worth; in Fig. 2 the plots of $\log \eta$ vs. $1/T$ give excellent straight lines.
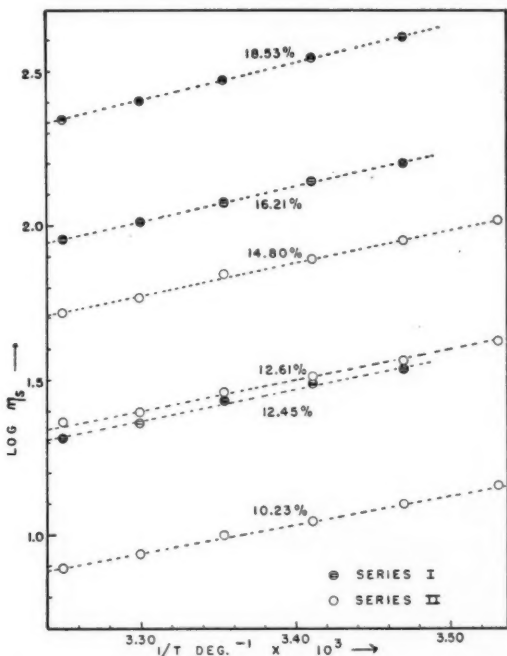
FIG. 2. *Viscosity as a function of temperature at various concentrations of solution.*

There is much less guidance offered by the literature in the choice of a suitable equation to relate viscosity to concentration. The equations that serve admirably in very dilute solution are not applicable with these concentrated solutions. Abernethy (1) in his excellent study of the viscosity of solutions of natural rubber in benzene favored the relation

$$\log \eta = k + k'C^{\frac{1}{2}}, \tag{3}$$

where C was the concentration of the solution expressed as grams of rubber per 100 ml. solution *at one fixed temperature*. This rather peculiar volume unit of concentration is really a weight unit; when, as in this instance, the density is independent of concentration, C is proportional to C_w, the concentration in weight per cent (gm. per 100 gm. solution). Abernethy's equation can therefore be rewritten in the form

$$\log \eta = k + k'' C_w^{\frac{1}{2}}. \tag{4}$$

Flory (15) independently, though much later, arrived at Equation (4) (also empirically) applying it to solutions of various linear polyesters. Spencer and Williams (23) have used it successfully with solutions of polystyrene in isopropyl benzene. As Fig. 3 clearly indicates, the equation holds for our system as well. Only data obtained at 15°, 25°, and 35° C. are plotted; those for 10°, 20°, and 30° give equally good straight lines.
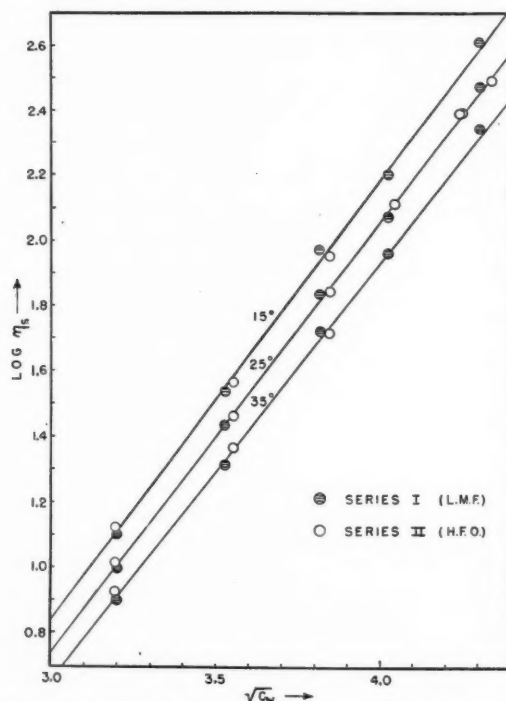
FIG. 3. *Viscosity as a function of concentration of solution at different temperatures.*

Examination of the data revealed that it was possible to summarize them all in one combined empirical equation, expressing the dependence of viscosity on temperature and concentration. From this equation,

$$\log \eta_s = -3.18_8 + \left(0.354 + \frac{285}{T}\right) C_w^{\frac{1}{2}} \tag{5}$$

(where η_s is the viscosity (Stokes) in poises, T is the absolute temperature, and C_w is the concentration in gm. per 100 gm. solution), values of the viscosity may be calculated which, with very few exceptions, differ from the observed values by not more than 5%. (In Fig. 3, the size of the circles corresponds to a precision of $\pm 4\%$.) Some of these calculated values are listed in Table III.

Actually we believe that this equation, though it embodies the systematic errors in our measurements, is more trustworthy than the individual observed values. In Fig. 3, the straight lines are *not* separately fitted to the points but are those with slopes and positions calculated from the combined equation. The excellent fit is therefore clear indication of the validity of the equation. The lines converge to a common point which, according to our equation in its equivalent form

$$\eta_s = 6.49 \times 10^{-4} \exp\left\{\left(0.815 + \frac{656}{T}\right) C_w^{\frac{1}{3}}\right\} \qquad (6)$$

corresponds to a viscosity of 0.00065 poises. In Fig. 2, the dotted lines have the slopes calculated from the equation. (The most inaccurate data in work of this nature are the concentrations; to give each line its calculated *position* as well as its calculated slope would be to emphasize the error in determining the concentration of the one solution used in obtaining all the points of one line.) It is interesting to note how well the observed variation of slope with concentrations (as shown by the *points*) agrees with that predicted by the equation.

The 'True' Viscosities

It will have been noted that in calculating viscosities no correction was made for the wall effect. Of the various correction factors that have been proposed (5), the most successful seems (2) to be that of Faxén (12) who proposed that the Stokes equation be corrected as follows:

$$\eta_F = 2/9gr^2 \left(\frac{\sigma - \rho}{v}\right)\left\{1 - 2.104\,\frac{d}{D} + 2.09\left(\frac{d}{D}\right)^3 - 0.95\left(\frac{d}{D}\right)^5\right\}, \qquad (7)$$

where d is the diameter of the ball, D the diameter of the fall tube. The value of this correction is illustrated by data obtained with a standard oil (furnished and calibrated by the Bureau of Standards—$\eta^{25°} = 8.84$ poises) and listed in Table IV.

TABLE IV

VISCOSITY OF STANDARD OIL

Ball diam., in.	d/D	Time of fall (average), sec.	η_s	η_F *
1/32	0.0365	40.2$_3$	9.7$_3$	8.9$_8$
3/64	0.0547	18.8$_4$	10.1$_4$	8.9$_6$
1/16	0.0732	11.1$_8$	10.4$_8$	8.8$_8$
1/8	0.147	3.5$_1$	13.1	9.1

* *We shall symbolize by η_F the viscosity value obtained by applying the Faxén correction, and shall refer to this value as a Faxén viscosity.*

Both Stokes and Faxén viscosities extrapolate to a value of $8.9_5 \pm 0.1$ poises at $d/D = 0$—see Fig. 4 (*a*). (This is the viscosity that would be determined if the walls of the fall tube were at infinite distance (2, 5).) With the Stokes
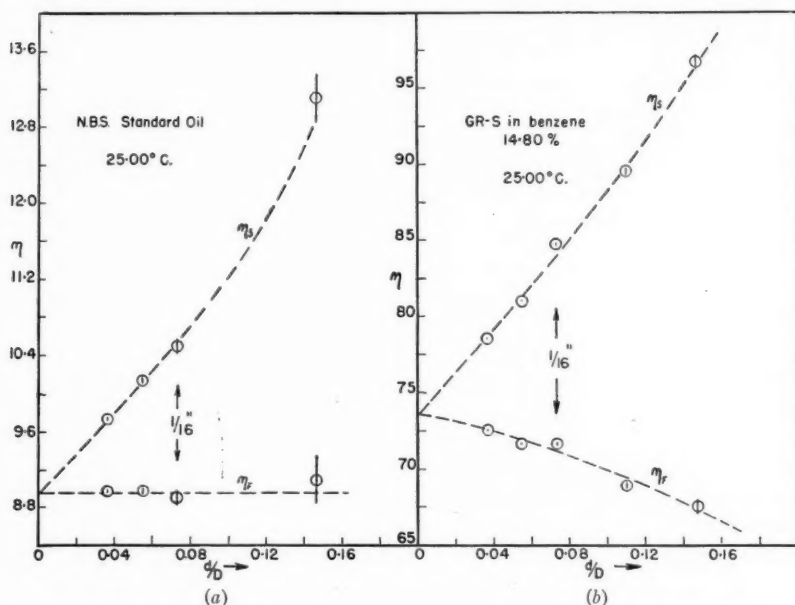
FIG. 4. *Apparent viscosity as a function of relative diameters of ball and tube d/D: (η_s, as calculated by the simple Stokes equation; η_f, as calculated by the Faxén modification of the Stokes equation).*

viscosities such an extrapolation is necessary if the 'true' viscosity is to be obtained, but the Faxén viscosities give a good approximation without extrapolation.

With the GR–S solutions, however, the Faxén viscosities are not equal to each other or to the 'true' viscosity. Balls of different diameter fall through a liquid with different velocities; the slower the fall the lower is the rate of shear. In a Newtonian liquid, such as the standard oil, the viscosity coefficient is independent of the rate of shear, but in solutions of GR–S the apparent viscosity decreases with increasing shear rate. (This is plainly indicated in measurements with a rotational viscometer.) The 'true' viscosity of such a liquid is the viscosity at zero rate of shear obtained by extrapolation. In Fig. 4 (*b*) are shown typical data obtained with balls of diameters 1/32 in., 3/64 in., 1/16 in., 3/32 in., and 1/8 in. falling through a GR–S–benzene solution of concentration 14.80% at 25.00° C. Although the Faxén viscosities fall away with increasing ball size (increasing rate of shear) the value obtained with the 1/16 in. ball is still a fair approximation to the extrapolated value. (Other experiments at 10° and 35° C. indicate that the deviation—

with the 1/16 in. ball—is generally of the order of 4%.)   Certainly the Faxén viscosity is in general much to be preferred to the Stokes viscosity, and we believe that even with these solutions a Faxén viscosity measured with the 1/16 in. ball gives a good measure of the 'true' viscosity.

The correction can be very simply applied to all our results.   The correction factor (Equation (7)) is independent of temperature and concentration; for a 1/16 in. ball in our apparatus it has the value 0.698.   Accordingly, Equations (5) and (6) become

$$\log \eta_F = -3.34_4 + \left(0.354 + \frac{285}{T}\right) C_w^{\frac{1}{2}} \tag{8}$$

and

$$\eta_F = 4.53 \times 10^{-4} \exp\left\{\left(0.815 + \frac{656}{T}\right) C_w^{\frac{1}{2}}\right\} \tag{9}$$

The correction of course does not affect the slopes of either the concentration or temperature lines.

It is worth emphasizing that there has been no need of differentiating between the results of Series I and Series II in evaluating the constants of the equation.   The one sample of GR–S was made in the plant months after the other, yet the concentrated solution viscosity behavior of the two was indistinguishable.   It does not follow, however, that the viscosity behavior of any butadiene–styrene copolymer, in solution in any solvent, could be expressed by our relation, though in view of the similar behavior of styrene solutions (23) it is reasonable to suppose that an equation of the same general type would be applicable.   For another polymer differing from normal GR–S only in molecular weight (not in more fundamental ways such as the proportion of 'bound' styrene) we could with some confidence predict, on the basis of the experience of Flory (15) with polyesters and Spencer and Williams (23) with styrene, that the viscosity temperature coefficient would, as with GR–S, have the value $B' = 285\ C_w^{\frac{1}{2}}$ (or $B = 656\ C_w^{\frac{1}{2}}$).

Activation Energy for Viscous Flow

Eyring and Ewell (9; 10; 11; 16, Chap. IX) have developed a theory of viscous flow of liquids that gives considerable significance to the viscosity temperature coefficient, i.e., to the constant B' in the equation $\log \eta = A' + B'/T$.   They write this equation in the form

$$\eta = A e^{\Delta E_{vis}/RT}, \tag{10}$$

where ΔE_{vis} is 'the viscosity energy' (9) or the activation energy for viscous flow (10), an energy quantity that is considered to include the energy required in the formation of a hole in the liquid into which the molecule (or the segment of it involved in the elementary process of flow) can move and the activation energy of the motion into the hole.   In low-molecular weight liquids (and in dilute *solutions* of high polymeric substances (15)) the whole molecule apparently is displaced in the unit flow process, but in the viscous flow of high polymeric substances the activation energies that have been observed (usually about 10 kcal. per mole) are much smaller than the energies that would be

required to form the large holes necessary to accommodate the entire molecule and to move the molecules into them. Instead, it seems probable (14, 15, 17) that long chain molecules flow by means of a series of movements of segments, the elementary flow process involving relative displacement of only a small section of the molecule. "The extraordinarily high viscosities of polymers are due to a lack of coordination between these essentially independent rearrangements of small chain sections" (15, 17).

Flory extended the theory to concentrated solutions of polymers; from the fact that the melt viscosity relation $\log \eta = A + K W_2^{\frac{1}{4}}$ (where W_2 is the weight fraction of polymer), which he had established for molten polyesters, was also valid for their concentrated solutions, he concluded that the mechanism of flow in concentrated solutions is the same as in the polymer itself. This same conclusion was reached on entirely different grounds by Baker, Fuller, and Heiss (3). If this concept is accepted as generally valid, it becomes possible to determine the value of $\triangle E_{vis}$ for a polymer by extrapolation of data obtained with concentrated solutions. Conversely, agreement between the value obtained by such extrapolation and that obtained directly by measurements on the pure polymer is strong support for the belief that in the concentrated solutions, as in the polymer, viscous flow involves successive displacements of relatively short segments of the polymer molecules.

Ferry (13) obtained a value of $\triangle E_{vis}$ for polystyrene by plotting $\triangle E_{vis}$, for solutions of various concentrations, against weight concentration and extrapolating linearly to 100% polymer. Spencer and Williams (23) preferred to average the values of $\dfrac{\triangle E_{vis}}{W_2^{\frac{1}{4}}}$. (The two methods are not equivalent; Ferry's line is drawn through the point $\triangle E_{vis} = 2.1^*$ at 0% polymer, whereas the procedure of Spencer and Williams corresponds to the extrapolation to $W_2 = 1$ of a line passing through the origin.) By these methods Ferry obtained a value of 12.8 kcal., Spencer and Williams one of 9.7; on pure (molten) polystyrene Nason (19) made measurements from which Spencer and Williams have calculated an activation energy of 15.5 kcal. per mole. These figures are given here to indicate the sort of agreement that may be expected.

Our data cover a relatively narrow range of concentrations and temperatures but are sufficiently precise to make irresistible the temptation to try a similar extrapolation. Our equation has been proved valid over a 10% concentration range; it implies the constancy of the ratio $\dfrac{\triangle E_{vis}}{C_w^{\frac{1}{2}}}$. If we were to make the bold assumption that it is also valid for the pure polymer, then the value of $\triangle E_{vis}$ for GR–S could be calculated as $(656\ C_w^{\frac{1}{2}})\ R$, where $C_w^{\frac{1}{2}} = 10$. The value so obtained is 13.0 kcal. per mole. The activation energies for flow directly observed for polymers of this type are usually of the order of 10 kcal. (17); for example that of natural rubber is 10.5 kcal.

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* The experimental value for pure benzene is 2.5 kcal. per mole (9).

(22*, 24) and that of polystyrene 15.5 kcal.† Our extrapolated value for GR–S—13.0 kcal.— is therefore a reasonable one; the fact that it is so is strong indication that the flow behavior of this synthetic rubber is much the same in or out of (concentrated) solution.

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* *Using the data of Mooney (18).*

† *After the proofs of this paper had been corrected and returned, a thorough investigation of viscosity–temperature relations for polystyrene and polyisobutylene was reported by Fox and Flory (J. Am. Chem. Soc., 70 : 2384, 1948). Over wide ranges of temperature "both polymers exhibit non-linear relationships between log η and 1/T". Apparent energies of activation for viscous flow were, however, calculated at various temperatures. Values (kcal.) for polyisobutylene were 13.2 at 100°, 13.7 at 50°, and 19.3 at 0° C. (as compared with our extrapolated value of 13.0 for GR–S —another rubbery polymer—at 25° C.). Corresponding values for polystyrene were greater, and the rate of increase in the value with decreasing temperature was greater, than for polyisobutylene: even for low-molecular-weight material (ca. 3700) they range from 27 at 100° to 37 at 88° C.*

KINETIC STUDIES ON THE FORMATION OF POLYBUTADIENE[1]

By W. Graham[2] and C. A. Winkler

Abstract

The growth rate of polybutadiene 'popcorn' is essentially the same in butadiene liquid and vapor, is proportional to the initial weight of seed used, and increases with increased active oxygen content of the seed and with increased temperature. Traces of nitric oxide and larger amounts of benzoyl peroxide and of iodine inhibit the growth of popcorn seed. Air also inhibits the growth. Popcorn formation is initiated in butadiene by benzoyl peroxide; the rate of initiation is increased by rusty iron and water and is a function of benzoyl peroxide concentration and temperature. Studies of 'gel' formation in liquid butadiene containing benzoyl peroxide indicate that the polymerization probably proceeds by a free radical mechanism, the rate being proportional to the square root of the benzoyl peroxide concentration. The growth of polybutadiene 'popcorn' appears to take place by relatively slow reaction of monomer with free radicals formed rapidly by decomposition of hydroperoxides in the seed.

Introduction

The majority of polymer used for the production of synthetic rubber on the American continent is obtained by the emulsion copolymerization of butadiene and styrene. In practice, the reaction is stopped after about 72% conversion of monomers, owing to formation of inferior quality polymer at higher conversions. Hence, recovery of unreacted monomers from the reaction system is an economic necessity. In the butadiene recovery unit there generally forms an insoluble, essentially pure, polybutadiene which fouls, and may swell sufficiently to damage, the distillation equipment. The object of the present work was to study the mechanism of formation and growth of this polymer with a view to obtaining data that might indicate a method of eliminating the costly nuisance from operation of polymerization plants.

Experimental and Results

Materials and Equipment

The butadiene used contained 98% 1,3-butadiene, the remaining 2% being butenes (material and analysis kindly supplied by Polymer Corporation, Sarnia). Inhibitor (*t*-butylcatechol) present in the material as received was removed by bubbling the gas through sodium hydroxide solution (2 *N*), after which the gas was dried over alumina and phosphorus pentoxide and stored at $-78°$ C. until used.

Butadiene was introduced into the reaction tubes by low temperature distillation. When necessary, the amount of gas introduced was determined by the familiar technique of measuring the pressure change in a standard

volume from which the gas was removed by condensation into the reaction tubes. During reaction the tubes were maintained at the desired temperatures by air or liquid thermostats.

Preliminary experiments on growth of polymer in the vapor phase were made by suspending a weighed sample of the polymer, contained in a small glass cup, from a calibrated phosphor bronze spring over liquid butadiene in a sealed tube. The increase in weight determined from the extension of the spring was assumed to be the sum of the increased polymer weight plus the weight of butadiene sorbed by the polymer. The weight of polymer formed during reaction was obtained by opening the tube, venting the butadiene and weighing the polymer residue. The values obtained for the amount of butadiene sorbed by the polymer appeared to be abnormally large and not reproducible. Subsequent experiments made on the growth rate of polymer in liquid butadiene containing a piece of phosphor bronze indicated that some reaction occurred, to form a green compound that partially inhibited the growth of polymer. The studies with phosphor bronze springs gave only qualitative results, which may be summarized briefly as follows:

(i) The curves obtained by plotting weight of polymer against time were almost linear initially, but the rate of growth fell off slowly with time.

(ii) Small amounts of oxygen added to the reaction tube decreased the rate of growth of polymer in butadiene vapor.

(iii) Small amounts of nitric oxide inhibited the growth markedly. Polymer treated in this manner was only slightly activated by exposure to air for a month.

(iv) Exposing the polymer to nitric oxide for 12 hr. partially inhibited its rate of growth in butadiene vapor.

(v) Polymer placed in a solution of bromine in carbon tetrachloride turned black after several days. Material treated in this manner did not react with butadiene.

(vi) Heating the polymer seed to 100° C. *in vacuo* for several hours markedly decreased its rate of growth in butadiene.

Satisfactory quantitative data were obtained in two ways: (*a*) by replacing the phosphor bronze springs with calibrated Pyrex glass spirals; (*b*) by direct dry weight method. The latter method required several reaction tubes, each containing 0.100 gm. seed and a known amount of butadiene, to obtain a single growth curve. At intervals, a tube was removed from the thermostat, vented, and the weight of polymer obtained after heating in a vacuum oven at 100° C. for 24 hr. to remove residual butadiene and its dimer.

Effect of Seed Weight on Growth Rate in Butadiene Vapor

Using the direct weight method, the growth in butadiene vapor at 75° C., of spherical pieces of polybutadiene weighing 0.05, 0.100, and 0.200 gm., was found to be linear with time up to sixfold increase of weight. The growth rates, determined from the slopes of the growth curves, are plotted against

initial seed weight in Fig. 1, to illustrate that the growth rate is proportional to the initial weight of seed.
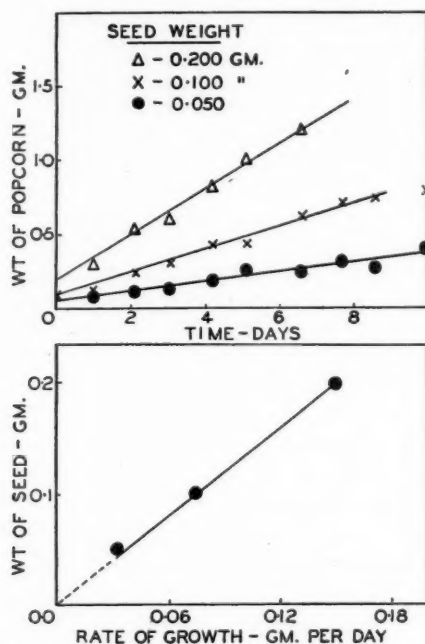
FIG. 1.   *Effect of seed weight on growth of popcorn at 75° C.*

Relative Growth Rates in Vapor and Liquid Phases, and Effect of Peroxide Content of Seed

Polybutadiene was reduced in size by grinding and the fraction passing 20 mesh and retained on 40 mesh was used for growth studies in the vapor and liquid butadiene at 75° C.   Both the calibrated spring and direct weight methods were used for growth rates in the vapor phase, while the direct weight method only was used for studies in the liquid phase.   The vapor phase data were corrected for sorbed butadiene by determining the dry weight of polybutadiene at the end of the experiment and applying a suitable correction to the weight data at different time intervals on the basis of the per cent butadiene sorbed by the polymer.   The initial weight of seed was 0.100 for measurements in both phases, but the various seeds used differed in peroxide contents, as determined by the method of Robey and Wiese (12).   This consisted of extracting 0.500 gm. of polymer with 25 ml. benzene for two days at 60° C. in an atmosphere of nitrogen.   An aliquot of the benzene extract was added to 25 ml. standard solution of ferrous chloride – potassium thiocyanate in absolute alcohol – chloroform solution, and the color compared in a Fisher electrophotometer with the color obtained by adding a known quantity of

ferric chloride hexahydrate to the standard solution. The peroxide values so obtained must be regarded as relative only, with an accuracy probably not better than 10% at 10 p.p.m. active oxygen (14).

Seeds of low peroxide contents were obtained by prolonged benzene extraction at 60° C. in an atmosphere of nitrogen.

The growth rates in vapor and liquid phases were found to be substantially the same for given seed material, within the limits of the techniques used. The amount of butadiene sorbed by the polymer was found to vary from 9.8% to 35.2%, but was generally of the order 20% to 30%.

The initial growth rates, analyses of popcorn seed, and percentage butadiene sorbed are summarized in Table I.

TABLE I

SUMMARY OF DATA FOR GROWTH OF BUTADIENE POPCORN IN LIQUID AND VAPOR PHASES AT 75° C.
Initial weight of seed, 0.100 gm.

Growth phase	Active oxygen in seed, $\% \times 10^2$	Butadiene sorbed, % by weight	Corrected initial growth rate, gm. per day
Vapor	0.2	30.9	0.03
Liquid and vapor	0.2	—	0.05
" " "	0.4	—	0.08
Vapor	0.6	22.6	0.03
Vapor	0.9	23.2	0.08
Vapor	1.2	35.2	0.03
Vapor	1.2	32.7	0.09
Liquid and vapor	1.9	—	0.11
Liquid	3.7	—	0.19
Liquid and vapor	7.2	20.2	0.23
" " "	11.5	27.4	0.22

In Fig. 2 the active oxygen content of the seed is plotted against the initial growth rate, to show, at least qualitatively, that the growth rate increases with increasing peroxide oxygen content of the seed.
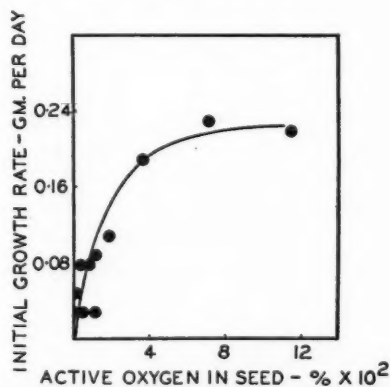
FIG. 2.   Relation of growth rate of popcorn to peroxide content of seed.   Temperature, 75° C. Initial weight of seed, 0.100 gm.

Effect of Seed Size on Growth Rate

Growth rates in liquid butadiene at 75° C. were determined with popcorn ground and sieved into fractions +10, −20 mesh, +20, −48 mesh and +60 mesh, with the results shown in Fig. 3.   The product from the finest seed was
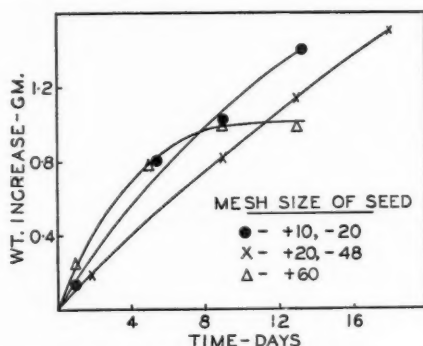
Fig. 3.   *Effect of surface on growth rate of popcorn at 75° C.   Initial weight of seed, 0.100 gm.*

a spongy mass, which retained its resilience in the absence of air, but became quite friable on exposure to air.

Growth of Popcorn in Liquid Butadiene Containing Benzoyl Peroxide

In liquid butadiene containing benzoyl peroxide, growth of popcorn seed was accompanied by production of a gel-like insoluble polymer, which swelled in benzene and toluene.   Separation of the gel from the popcorn was not feasible, hence the weight of popcorn was determined by correcting for the weight of gel produced, as determined in experiments with unseeded butadiene containing benzoyl peroxide.   By merely venting unreacted monomer from the unseeded reaction tubes, followed by heating *in vacuo* at 100° C. the weight of gel formed was readily obtained.   Typical rate data for the formation of polybutadiene gel at 75° C. are plotted in Fig. 4, while in Fig. 5 are graphs to illustrate the relation between benzoyl peroxide concentration and fraction of monomer polymerized after five days at 75° C. and after 1.5 days at 100° C.   Data are included for one series of experiments in which 0.006% by weight of air was added.   From data for the formation of gel plus popcorn in seeded samples were subtracted the corresponding values for formation of gel alone, to yield the growth curves of Fig. 6 for popcorn alone in butadiene containing benzoyl peroxide.

Growth of Butadiene–Styrene Popcorn in Liquid Butadiene

Butadiene–styrene popcorn (0.100 gm. seeds) containing 2, 5, 8, and 25% combined butadiene was grown in liquid butadiene with the results shown in
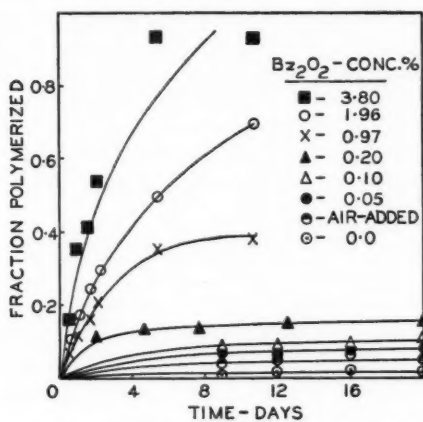
FIG. 4.   *Formation of polybutadiene gel at 75° C.*
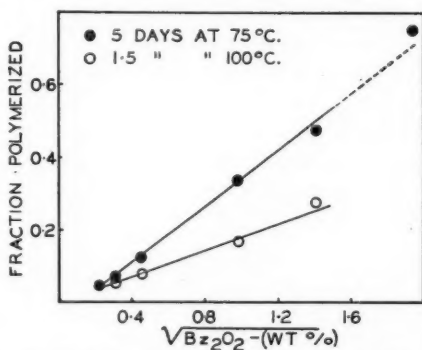
FIG. 5.   *Effect of initial benzoyl peroxide on formation of gel.*
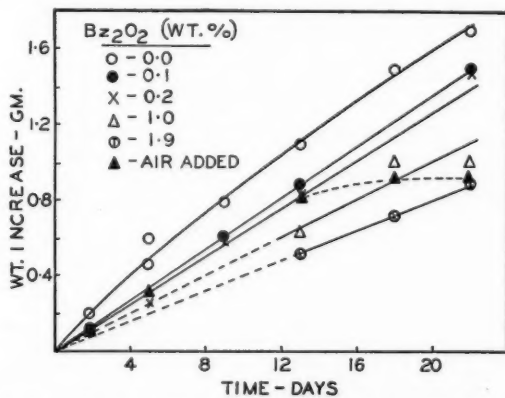
FIG. 6.   *Effect of initial benzoyl peroxide on growth of popcorn.*

Fig. 7.   The slopes of reaction–time lines, plotted against per cent butadiene in the seeds used, give a linear relation, indicating that the rate of growth is proportional to the number of butadiene units in the seed.
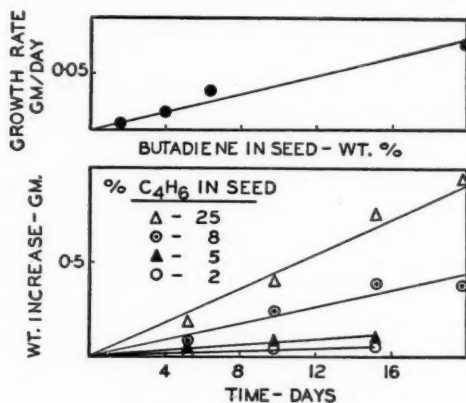
FIG. 7.   *Growth of butadiene–styrene popcorn in liquid butadiene at 75° C.*

Effect of Temperature on the Growth Rate of Popcorn in Butadiene

Growth studies were made at 50°, 75°, and 100° C., using liquid butadiene seeded with +20, −48 mesh popcorn.   The results, plotted in Fig. 8, are too few to permit satisfactory calculation of an activation energy.
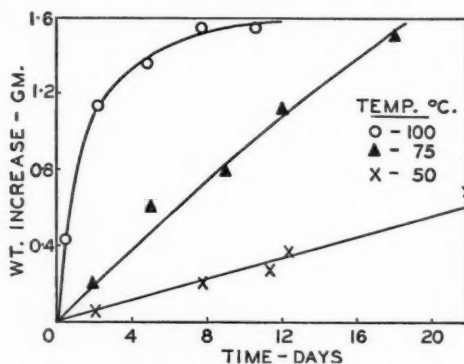
FIG. 8.   *Effect of temperature on the growth rate of popcorn in liquid butadiene.   Initial weight of seed, 0.100 gm.*

Initiation of Popcorn in Unseeded Liquid Butadiene

Previous work (7, 10) has indicated that active oxygen is necessary for popcorn initiation and that a water interface, especially in the presence of rusty iron, accelerates its growth.   The present study was made with butadiene containing benzoyl peroxide in concentrations 0.1, 0.2, 0.5, 1.0, 1.6, 2.0,

4.0, and 6.0% by weight, at room temperature and at 75° C. Four tubes were prepared at each catalyst concentration: one tube contained only liquid butadiene plus benzoyl peroxide; two contained benzoyl peroxide in butadiene plus a rusty nail; the fourth contained benzoyl peroxide in butadiene, plus a rusty nail and 1 ml. water. The tubes were examined periodically during a period of 100 days for the presence of popcorn. Without attempting to record the observations made, the conclusions drawn may be summarized as follows:

(a) There is an optimum concentration of benzoyl peroxide for popcorn initiation, this concentration being about 1% at 75° C., and 4% at room temperature.

(b) Initiation of popcorn was accelerated by rusty iron and this acceleration was more marked with water plus iron. Samples containing water plus iron (and benzoyl peroxide) were almost completely converted to popcorn before samples containing iron (plus benzoyl peroxide) showed any significant popcorn formation, while the latter, in turn, were partially polymerized before popcorn was visible in samples containing only benzoyl peroxide.

. (c) Visible amounts of popcorn were formed in about one week at 75° C., under optimal conditions (1% benzoyl peroxide, iron, and water added), but most of the monomer was converted to 'tacky' gel, rather than to popcorn. At room temperature, on the other hand, visible popcorn was formed only after about one month (under optimal conditions), but essentially complete transformation of monomer to popcorn occurred during a three month period.

Inhibition of Popcorn Polymer Growth

Nitric oxide, to the amount of 0.02% by weight of butadiene present, was found to inhibit, almost completely, the growth of polybutadiene seed in liquid butadiene containing benzoyl peroxide at 75° C. during a period of one month. After two months, samples containing less than 0.05% nitric oxide had grown slightly, but with larger amounts of nitric oxide (up to 0.08%) no significant growth occurred during a similar period.

Iodine was found to be much less effective than nitric oxide for inhibiting popcorn growth; popcorn grew slowly in 5 gm. samples of butadiene containing 0.2% by weight iodine.

Discussion of Results

Mechanism of Popcorn Growth in Butadiene

All the rate curves obtained in the present investigation indicate an almost linear relation between the weight of popcorn and the time of contact with butadiene, the initial slope of these curves being directly proportional to the initial weight of popcorn seed and a function of the peroxide content of the popcorn.

These observations are not in agreement with the work of Welch *et al.* (14), who reported that the rate of growth, at any time, is directly proportional to the weight of popcorn, giving a logarithmic expression for the rate curve. A possible explanation of this discrepancy is that their experimental data, which were obtained by observing the rate at which the volume of butadiene decreased in a reaction tube containing popcorn in the vapor phase, are in error as a result of polymerization in the liquid phase causing a volume change, which would be attributed to popcorn growth.

The dark growth of the insoluble photopolymer of methyl methacrylate, which was investigated by Melville (9), resembles butadiene popcorn growth in that the growth curves are similar and both polymerizations are inhibited by iodine. However, his proposed mechanism (addition of monomer to an activated double bond at the end of the molecule) does not explain the increase in growth rate with peroxide content of popcorn, the inhibiting effect of oxygen, or the marked decrease in growth rate as a result of heating popcorn *in vacuo* (insoluble polymethyl-methacrylate was unaffected by similar heating).

The ease with which insoluble popcorn-type polymers of chloroprene (1), isoprene (5), and butadiene (3, 4) can be initiated by ultraviolet light, which produces free radical chains, suggests a free radical mechanism for popcorn propagation. The continued formation of insoluble polymer, by the addition of monomer to active centers on the polymer present, following removal of the source of radiation, is analogous to the growth of popcorn in butadiene. Finally, the inhibiting effect of nitric oxide (which is well known for its ability to stop free radical reactions by terminating the active chains) leads to the conclusion that the mechanism of popcorn growth is the successive addition of monomer molecules to free radicals on the surface, or in the body of the popcorn seed. It should be noted that iodine is also known to inhibit free radical reactions, and in fact has been used to estimate free radicals by Medvedev (8).

The negligible effect of increased superficial surface, by size reduction of the seed, on the initial growth rate of popcorn in butadiene indicates that butadiene popcorn resembles a gel—rather than a true solid—with a very extensive surface, but limited swelling owing to cross-linking. If this be true, polymerization probably takes place throughout the body of the seed and not at the superficial surface.

Growth within a gel structure in this way would afford a ready explanation of the tremendous growing force exerted by the polymer, which would be hard to account for if the growth occurred only at the visible surface.

The large amount of butadiene sorbed by the popcorn also supports a gel structure for it.

It seems very probable that the active radicals initiating the reaction chains are formed on and in the seed and not in the monomer surrounding it; otherwise, the equality of the rates of growth in the liquid and vapor phases, with given seed material, would seem to be fortuitous. Initiation of the chains in

the monomer followed by termination on the surface of the popcorn would yield a rate of reaction dependent on the surface area of popcorn, which has not been observed.

If a free radical chain mechanism be assumed for popcorn growth, a kinetic interpretation of the reaction must account for the initiation, propagation, and termination of the free radical chains.

It does not seem possible that the initiation of active centers can be explained completely by the presence of free radicals as such in the seed. This would fail to explain the observation that exposing the seed to nitric oxide for 24 hr. does not result in complete inhibition of growth. Furthermore, if the only source of active centers is those free radicals remaining on the parent material, a progressive reduction in the rate of growth would be observed in succeeding generations of popcorn, since only a fraction of the material is used as seed; this, however, has not been observed.

The plot of rate of popcorn growth against its peroxidic oxygen content (Fig. 2) shows that the rate of growth increases with an increase in peroxidic oxygen. This suggests that free radicals arise from decomposition of peroxide groups, as postulated by Kharasch (6).

Further support for this mechanism of initiation is given by the linear relation between the per cent butadiene in seed of butadiene–styrene popcorn, and the rate of its growth in butadiene (Fig. 7). Since only butadiene contributes aliphatic double bonds to this type of polymer, and only methylene groups adjacent to double bonds form peroxides (2), proportionality between the rate of growth and butadiene content would correspond to proportionality between the rate of growth and the peroxide content, provided, of course, that all of the samples had the same opportunity to react with oxygen.

Assuming, on the basis of the above evidence, that free radicals are formed on popcorn by decomposition of peroxides and that growth of popcorn involves successive addition of sorbed monomer molecules to these free radicals, the rate of growth should be directly proportional to the number of free radicals and the concentration of sorbed butadiene. If the sorbed butadiene is assumed to be present in relatively large excess, and its concentration therefore taken as essentially constant, the rate expression is:

$$\frac{dw}{dt} = k_2 n , \tag{1}$$

where n is the number of free radicals in the seed, w is the weight of popcorn at time t, and k_2 is the rate constant.

Since the activity of free radicals results from the loss of a valence electron, it is difficult to imagine a chain terminating reaction that does not involve interaction between two free radicals to form a stable covalent bond. Some evidence for termination by interaction of two growing radical chains is given by the rate curves for different mesh seeds. Although these curves display approximately equal initial growth rates, after several days the rate of propagation of 60 mesh popcorn falls off very rapidly. The resulting polymer

from this seed differs from that of the coarser seeds in that the individual particles are bound together so that the mass resembles a sponge rubber. This fact and the decreased rate of growth may be explained by reaction between growing chains on adjacent particles which would decrease the number of growing chains and cause the observed inter-particle bonds.

There are two possible ways in which termination by interaction between radicals could take place; one being direct reaction between two growing chains attached to the surface, the other being reaction between unattached free radicals (arising from chain transfer reactions between chains attached to the surface and sorbed monomer) and other growing chains. It is impossible to determine which is the main terminating reaction from the available experimental data; it would be expected that the probability of reaction between the chains attached to the surface would be low, owing to their limited mobility on the surface, as compared with that for termination by the more mobile unattached free radicals.

On the basis of the above assumptions regarding the mechanism, the growth reactions may be represented by the following general equations:

1. Initiation: $ROOH \xrightarrow{k_1} R^*$

2. Propagation: $R^* + Bd \xrightarrow{k_2} RBd^*$

$$RBd_n^* + Bd \xrightarrow{k_2} RBd^*_{n+1}$$

3. Cessation: $RBd_n^* + RBd_m^* \xrightarrow{k_3} R_2Bd_{m+n}$
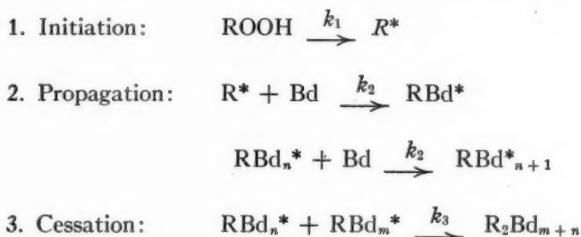
where ROOH is a hydroperoxide on the popcorn, R^* is a free radical, and Bd is a butadiene molecule.

Since the experimental evidence indicates that growth of the popcorn takes place throughout the body of the popcorn seed, it will be assumed, as a first approximation, that the seed acts as a solvent for the polymerization and concentrations may be expressed per gram of popcorn. The concentration of free radicals will then be n/w.

If C represents the number of peroxide groups on the seed at any time, then since their decomposition to yield free radicals was assumed to be first order with respect to the peroxides:

$$\frac{-dC}{dt} = k_1 C .$$

Assuming that free radical chains are terminated by a reaction second order with respect to the total number of free radical chains, the total rate of change of free radicals, given by their rate of formation minus their rate of termination, is:

$$\frac{1}{w} \cdot \frac{dn}{dt} = \frac{k_1 C}{w} - \frac{k_3 n^2}{w^2} .$$

The marked reduction in growth rate resulting from heating popcorn seed indicates that the decomposition of peroxides is a relatively rapid reaction. In the light of this it would be expected that the first term on the right-hand side of the above equation becomes negligible relative to the second after a short time, and the equation will reduce to:

$$\frac{dn}{dt} = \frac{-k_3 n^2}{w} .$$ (2)

Combining Equations (1) and (2) the following differential equation is obtained:

$$\frac{d^2 w}{dt^2} + \frac{k_3}{k_2 w}\left(\frac{dw}{dt}\right)^2 = 0 .$$

The solution for this equation gives:

$$\frac{dw}{dt} = \frac{C_1}{w^{k_3/k_2}} = k_2 n.$$ (3)

Since the peroxide decomposition was assumed to be rapid, it will further be assumed that the free radicals are a maximum at zero time and equal the original number of peroxide groups C_0. The integration constant C_1 in Equation (3) is then:

$$C_1 = k_2 w_0{}^{k_3/k_2} n$$

$$= k_2 w_0{}^{k_3/k_2} C_0 ,$$

where w_0 is the weight of popcorn seed used.

Putting this value of C_1 in Equation (3) and integrating between the indicated limits:

$$\int_{w_0}^{w_t} w^{k_3/k_2} dw = k_2 w_0{}^{k_3/k_2} C_0 \int_0^t dt$$

$$\frac{k_2}{k_2 + k_3}\left(w_t{}^{\frac{k_2+k_3}{k_2}} - w_0{}^{\frac{k_2+k_3}{k_2}}\right) = k_2 w_0{}^{k_3/k_2} C_0 t .$$ (4)

If the postulates regarding the mechanism are correct, Equation (4) must be consistent with the following experimental observations:

(1) The rate of growth is proportional to the initial weight of seed used.

(2) The shape of the growth curves.

(3) The shape of the curve for peroxide oxygen plotted against the initial rate of growth of popcorn.

In Fig. 9 is shown a typical plot of the logarithm of the rate of popcorn growth against the logarithm of the weight of popcorn corrected for sorbed butadiene. The resulting relation is essentially linear as predicted from the

differential form of Equation (4). From three such plots, for popcorns of closely similar peroxide contents (*ca.* $1 \times 10^{-2}\%$) a value of 0.25 was obtained as a rough estimate for the ratio k_3/k_2.
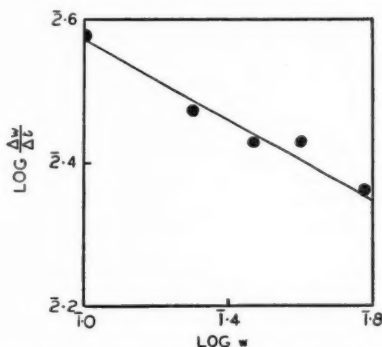
FIG. 9.   *Relation between rate of growth and weight of popcorn at 75° C.*

The differential form of Equation (4) predicts a linear relation between C_0 (the initial number of peroxide groups) and the rate of growth. Since C_0 is directly proportional to the initial weight of seed, the rate of growth should then be directly proportional to the initial seed weight. This is true experimentally as shown in Fig. 1, where the rate of growth for different weights of seed from the same source (i.e., having the same peroxide analysis) is plotted against the weight of seed.

The curve of initial rate of growth plotted against peroxide content of the seed (Fig. 2) is not linear as predicted by Equation (3), this deviation from linearity being much larger than would be caused by experimental error. The curve does, however, appear to be linear initially, but falls off rapidly at high peroxides. This might indicate that at high peroxide contents additional chain breaking reactions can occur, or perhaps the sorption of butadiene is not sufficiently rapid to maintain its concentration approximately constant at high peroxide levels.

In Fig. 10 values of $w^{1.25}$ (corrected for sorbed butadiene) are plotted against time, using representative data for growth of 20–48 mesh popcorn at 75° C. in both the liquid and vapor phases. The resulting relations, which are for two different seed materials, are linear as predicted by Equation (4). If the proposed mechanism is correct, the negligible induction period in these curves indicates that the peroxide decomposition is a rapid reaction, as assumed in deriving Equation (4), and that the free radicals, therefore, have a relatively long life in the popcorn. This indicates that their reaction with butadiene proceeds much more slowly than is usually assumed in free radical initiated polymerizations.

Other possible mechanisms have been considered in an effort to account for the data obtained. These are:

(1) Slow decomposition of peroxides to form free radicals that were then removed by a reaction first order with respect to free radicals.

(2) Slow decomposition of peroxides to form free radicals that were then removed by a second order reaction.
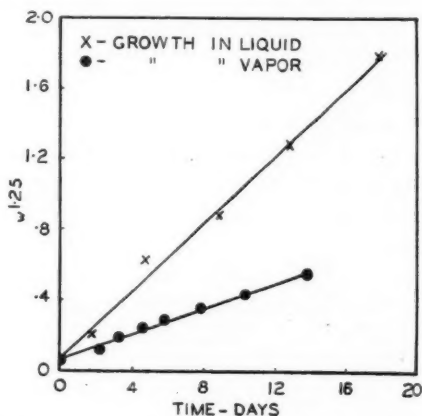
FIG. 10. *Typical relations for (Popcorn weight)$^{1.25}$ plotted against time.*

In both of these cases it was assumed that a steady state was attained at which the rate of initiation of radicals was equal to their rate of removal. The equations obtained on the basis of these assumptions do not fit the experimental data as well as those developed above.

Initiation of Popcorn Polymer in Liquid Butadiene

The results obtained in this study indicate that benzoyl peroxide, or some other source of free radical chain initiators, is essential for the formation of popcorn in liquid butadiene. The presence of rusty iron, and rusty iron plus water, accelerates initiation of popcorn when benzoyl peroxide is used.

These observations are in agreement with those of Welch *et al.* (13, 14).

It has also been found that there is an optimum concentration of benzoyl peroxide for popcorn initiation in butadiene. The optimum concentration was found to be dependent on the reaction temperature; at 75° C. it was approximately 1% benzoyl peroxide, and at room temperature, 4% benzoyl peroxide.

The problem of the mechanism of popcorn initiation is very complex, and no satisfactory explanation has been advanced to account for it. Formation of insoluble nuclei as the initial step is agreed upon by most investigators.

The transformation of a growing chain, which normally would result in a large soluble molecule, or one of the glassy gel type which is swollen by solvents, to a non-swelling, insoluble nucleus, is the difficult step to explain.

It is undoubtedly true that it must involve chain branching and cross-linking, but since these steps also take place in normal polymerization it seems that the difference between the formation of popcorn and normal polymer is one of degree only. The resulting nucleus once formed and containing free radical active centers protected from termination by outside radicals because of its cross-linked structure should continue to grow for a long time.

The existence of an optimum catalyst concentration shows that a minimum number of reaction chains must be formed for nuclei initiation, while at concentrations above this optimum the number of chains present is sufficiently large to cause termination before chains of insoluble proportions are reached. As a result, the bulk of the monomer will be converted to non-popcorn type polymers.

The ability of iron in the presence of water to catalyze the formation of insoluble nuclei is difficult to explain. Since benzoyl peroxide is essential and these materials are only accelerators, it is not unreasonable to suppose that the decomposition of benzoyl peroxide is catalyzed by a rusty iron surface; the increased accelerating action of water may be a result of hydrolysis of benzoyl peroxide to form compounds that decompose more readily to free radicals than does benzoyl peroxide.

Formation of Polybutadiene Gel in Liquid Butadiene Containing Benzoyl Peroxide

It is strongly indicated by the linear relation between the rate of gel formation and the square root of the peroxide concentration, shown in Fig. 5, that the benzoyl peroxide initiated polymerization of liquid butadiene proceeds by a free radical mechanism, in which the radicals are generated by a first order decomposition of benzoyl peroxide, and are removed by a second order termination of the radical chains.

If it is assumed that this is the mechanism, an analysis identical with that proposed by Price (11) for d-S-butyl-α-chloroacrylate yields the following expression for the rate of monomer disappearance:

$$\frac{- d[M]}{dt} = k' \, [\text{Catalyst}]^{\frac{1}{2}} \, [M], \tag{5}$$

where M = the butadiene concentration.

Since this is a bulk polymerization and involves a considerable volume decrease, concentrations will be expressed as per cent by weight instead of on the conventional molar basis. This avoids the necessity of introducing a term for the rate of volume change.

If P represents the fraction of butadiene polymerized, and the amount of benzoyl peroxide present at any time is $C_0 e^{-k_4 t}$ (from the equation for a first order decomposition, C_0 being the initial concentration of catalyst) the rate of polymerization is then given by substituting into Equation (5)

$$\frac{dP}{dt} = k' C_0^{1/2} e^{-\frac{k_4 t}{2}} (1 - P)$$

where $(1 - P)$ = fraction of butadiene monomer at time t.   Integrating:

$$\int_0^P \frac{dP}{1 - P} = k' C_0^{1/2} \int_0^t e^{-\frac{k_4 t}{2}} \; dt$$

$$- \ln (1 - P) = \frac{2k'}{k_4} C_0^{1/2} \left(1 - e^{-\frac{k_4 t}{2}} \right) \tag{6}$$

If the constants in Equation (6) are evaluated from the rate curves in Fig. 4, the following equation is obtained for polybutadiene gel formation at 75° C.:

$$\text{Log}_{10} (1 - P) = -0.684 C_0^{1/2} (1 - e^{-0.072 t}).$$

In Fig. 11, P as calculated from this equation, and as determined experimentally, is plotted against time for gel formation at benzoyl peroxide concentrations of 3.80, 2.0, and 1.0%; these curves show good agreement between calculated and experimental results for the initial part of the reaction.
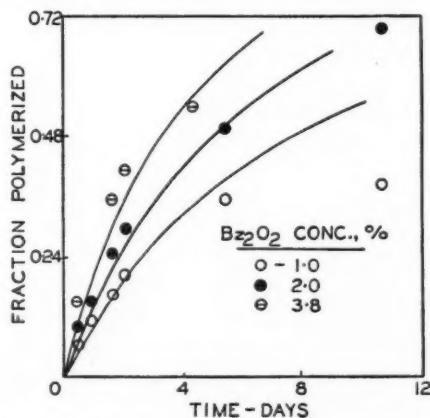
FIG. 11.   *Comparison of observed and calculated rates of formation of gel.*

The agreement with experiment in studies made at lower peroxide concentrations is not as good, possibly owing to the action of impurities which could cause a relatively large error at the low peroxide concentrations.

The growth data for popcorn in butadiene containing benzoyl peroxide are not sufficiently accurate to warrant any quantitative development.   They show, qualitatively, that the growth of popcorn is retarded by benzoyl

peroxide.   This is consistent with the proposed mechanism, the retardation of popcorn growth being caused by termination of popcorn chains by free radicals from the benzoyl peroxide decomposition.

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THE CATALYTIC ACTION OF ALUMINUM SILICATES

III. THE CONVERSION OF 1,1-DIPHENYLETHANE TO STYRENE OVER MORDEN BENTONITE[1]

By Maurice Morton[2] and R. V. V. Nicholls

Abstract

Optimum conditions for the vapor phase conversion of 1,1-diphenylethane to styrene and benzene over activated Morden bentonite have been found to be a temperature of 600° C., rapid feed rates, and the use of water vapor as diluent. Ethylbenzene has been found in the reaction products as a hydrogenation product. Styrene content has been found to be dependent directly upon vapor velocity while the conversion efficiency was found to be related directly to the use of water vapor as an inhibitor of carbon deposition on the catalyst.

Introduction

The rise of the synthetic rubber industry has naturally aroused increased interest in methods of production of one of its most important raw materials, styrene. Although the Dow process for the catalytic dehydrogenation of ethylbenzene is today predominant, many attempts have been made during the last few years to develop other processes either from the viewpoint of greater efficiency, or of auxiliary supply of this strategic material. One of these, which has recently been developed by the Dominion Tar and Chemical Company of Montreal (14), involves the pyrolysis of 1,1-diphenylethane and analogous compounds over a clay catalyst. The diphenylethane is apparently available as a by-product of the condensation of benzene and ethylene to ethylbenzene, or it can be directly synthesized through a condensation of benzene with acetaldehyde (5, 12). Since the initial results of this process appeared promising, it was considered worth while to investigate it more thoroughly, from the viewpoint of the mechanism of the reaction and the use of more active catalysts.

Only scant reference can be found in the literature to the pyrolysis of 1,1-diphenylethane. In 1873 Goldschmiedt (7) passed this compound through a pumice filled tube kept over red hot coals, and obtained mostly unchanged material with small amounts of stilbene. Radziewanowski (10) heated 1,1-diphenylethane with aluminum chloride and isolated some 9,10-dimethyl-9,10-dihydroanthracene as a product. He postulated the following mechanism

$$(C_6H_5)_2CHCH_3 + HCl \longrightarrow C_6H_5CHClCH_3 + C_6H_6$$
$$2C_6H_5CHClCH_3 \longrightarrow 2HCl + C_{16}H_{16}.$$

No further work was apparently done along these lines until 1940, when Sheibley and Prutton (13) pyrolyzed this hydrocarbon in a silica tube, non-catalytically at 676° to 702° C. in the presence of carbon dioxide. They obtained approximately 20% yield of converted products, consisting mostly of benzene and toluene, with a minor quantity of styrene.

Recently Han-Ying Li (8) studied the pyrolysis of 1,1-diphenylethane both non-catalytically and over several catalysts, in an atmosphere of nitrogen at low pressures. In the non-catalytic pyrolyses he obtained no reaction at temperatures up to 600° C., formation of some benzene and styrene between 600° and 700° C., and heavy carbonization at 800° C. Using three different catalysts, at 600° C., he obtained the following results:

Catalyst	Products
Nickel and zinc oxide	1,1-Diphenylethylene and stilbene
Aluminum oxide and zinc oxide	1,1-Diphenylethylene and styrene
Acidic white clay	Ethylbenzene and benzene.

No information is available concerning the yields obtained.

Dreisbach (4) has recently patented a process whereby 1,1-diphenylethane is pyrolyzed at temperatures of 200° to 350° C. in contact with aluminum chloride, to yield ethylbenzene and benzene. This may or may not be a vapor phase reaction, since the boiling point of the diphenylethane is about 270° C.

In addition to the above work, there is, of course, the process investigated by the Dominion Tar and Chemical Company (14), whereby 1,1-diphenyl-ethane was pyrolyzed over kaolin, at about 500° C., with water as diluent, to yield mainly styrene and benzene, with minor amounts of ethylbenzene.

The catalyst that was chosen for investigation was Morden bentonite, a Canadian clay mined by the Pembina Mountain Clay Company at Morden, Manitoba. It is essentially a bentonite of the montmorillonite type characterized by a rather high percentage of combined water and low percentages of alkaline earth substituents. Deans (3), and Wasson (15), and Bourns (1) have investigated the efficacy of this catalyst for different types of vapor phase reactions. They found that its activity can be much enhanced by treatment with a mineral acid, the usual method of activation for catalysts of this type. For a range of different reactions, it was found that Morden bentonite acted mainly as an aid to fission of the carbon-to-carbon linkage, as well as a dehydration catalyst. These results are in general agreement with the known behavior of montmorillonite catalysts, which are finding wide-spread application for petroleum cracking.

Experimental Procedures

Since 1,1-diphenylethane has a boiling point of 266° C. it was necessary to construct a furnace that would be capable of handling a high boiling liquid, and at fast rates if so desired. The apparatus assembled is shown in Fig. 1.

The furnace, K, was specially designed after some experimentation. It consists of three 550 w. cylindrical heaters, wound on 12-in. alundum cores (Hoskins FD-303 oversize) and placed end to end so as to extend to a height
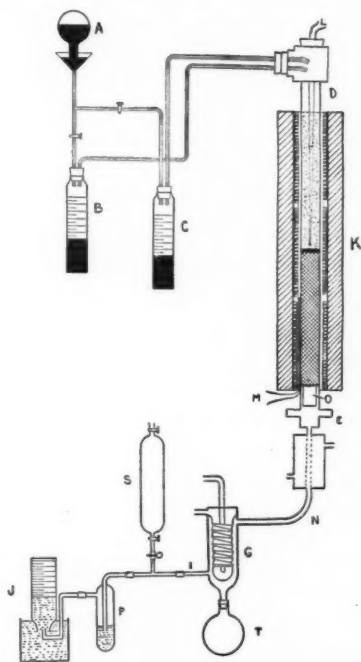
FIG. 1. *Catalytic pyrolysis apparatus. A = Mercury reservoir. B, C = Diphenyl-ethane and water reservoirs. D = 1 in. iron pyrolysis tube, 42 in. long. K = Insulating jacket. L = Internal thermocouple wire. M = External thermocouple wire. N = water-jacketed delivery tube (½ in. copper). G = Frederich condenser. S = Gas sampling bulb. J = Gasometer.*

of 36 in.   These heaters are surrounded by a 36 in. section of asbestos high temperature pipe covering, $2\frac{1}{2}$ in. thick, for insulation purposes. The top heating element is controlled by a separate rheostat to yield any desired heat input for vaporization and preheating of the vapors.   The two elements below are wired both in series and in parallel and are controlled through a suitable rheostat to yield any desired temperature for the catalytic pyrolysis.

The Morden bentonite was received in the form of a fine powder readily passing through a 200 mesh screen.   It was activated according to the method outlined by Gallay (6) using the following conditions.   The raw bentonite was treated with a boiling 20% solution of sulphuric acid for three hours. The weight of concentrated acid used was approximately half of the weight of bentonite treated.   Care was taken to keep the acid at the proper concentration by periodically replacing any evaporated water.   Subsequently,

the mixture was cooled, diluted to three times its original volume, filtered, and thoroughly washed. After drying the wet cake at 110° C. overnight, it was broken into lumps and screened to retain the material between the 4 and 8 mesh screens.

The 1,1-diphenylethane was obtained from the Dow Chemical Company of Midland, Michigan. As received, it had a faint yellow color and a boiling range of 265° to 268° C. It was fractionally distilled under reduced pressure in a Stedman column until a water-white liquid of constant boiling point and refractive index was obtained. The physical constants were all found to be lower in value than those recorded in the literature, the most recent reference being dated 1923. The constants were as follows:—

Boiling point   266°C. (760mm.) 134° C. (12mm.)

Specific gravity (d_4^{25}) 0.9928

Refractive index $(n_D^{14.5})$ 1.5714

The pyrolysis tube was packed as shown in Fig. 1, a 110 gm. quantity of 4 to 8 mesh activated Morden bentonite occupying a space of 18 in. (270 cc.), while an additional height of 15 in. above the catalyst was occupied by the pumice. A forerun of about 30 cc. of the starting material was usually required before equilibrium conditions were reached. A run usually required about 70 cc. of material.

A gas analysis was carried out whenever the amount of gaseous products obtained was equal to or greater than 10 cc. for each cubic centimeter of starting material. The liquid products, separated from any water, were given a preliminary distillation resulting in three definite fractions, viz.:—Fraction I, boiling below 150° C.; Fraction II, boiling between 260° C. and 280° C.; and residue. The lower boiling fraction was then fractionally distilled in a small glass-helices column, and the components identified by means of their boiling points, refractive indices, and densities. Since it was found that this distillation led to polymerization of some of the styrene in the fraction below 150° C., the styrene was determined separately by means of a bromination technique according to Williams (16). The fraction boiling between 260° and 280° C. was identified as consisting mainly of unchanged 1,1-diphenylethane. No attempt was made to identify the small proportion of high-boiling tar that remained as a residue, and usually comprised about 2 or 3% of the original charge.

Reactivation of the catalyst between successive runs was carried out by passing air over the catalyst at 550° to 600° C. This treatment gave reproducible results in catalyst activity.

The following variables were investigated:—

(1) Effect of pyrolysis at 500° C. on catalyst activity,

(2) Variable feed rates at temperatures of 400° to 650° C.,

(3) Effect of water and nitrogen diluents on pyrolysis at 500° C.,

(4) Pyrolysis of styrene–benzene mixtures at 500° C.

The use of water as a diluent was introduced in this investigation, since it was found at the outset that the presence of water vapor greatly enhanced the production of styrene.

Results and Discussion

(1) *Activity of Catalyst at 500° C.*

The effect of pyrolysis on catalyst activity is shown in Table I.

TABLE I

CATALYST ACTIVITY AT 500° C.

Run No.	11	12	13	14	20	23	24
Feed rate, moles per hour per 100 ml. of catalyst							
Diphenylethane	0.122	0.122	0.122	0.122	0.122	0.366	0.366
Water	1.24	1.24	1.24	1.24	1.24	3.72	3.72
Vapor products, liters per mole of diphenylethane	1.82	1.46	0.97	0.97	0.85	0.80	0.80
Main liquid products, % by weight of original material							
Benzene	38.6	20.5	31.8	33.6	32.2	27.8	28.5
Ethylbenzene	34.1	15.0	21.2	20.1	21.0	14.0	9.4
Styrene	3.7	6.6	10.9	11.2	12.1	14.0	18.3
*Total	76.4	42.1	63.9	64.9	65.3	55.8	56.2
% of theoretical yield styrene	6.5	11.6	19.1	19.6	21.2	24.5	32.0

Catalyst condition:—Run 11. Freshly activated. Run 12. Not reactivated after Run 11. Run 13. Reactivated after Run 12. Run 14. Reactivated after Run 13. Run 20. After nine runs and reactivations. Run 23. Freshly activated. Run 24. Reactivated after Run 23.

* *Remainder mainly unconverted 1,1-diphenylethane.*

It is apparent that the pyrolysis of 75 gm. of starting material at a relatively low feed rate deactivated the catalyst to such an extent that the subsequent run resulted in a conversion of diphenylethane to lower boiling products of only 42.1% as against 76.4% in the case of the fresh catalyst. Reactivation of the catalyst raised the conversion, but only up to 64–65%. When a faster feed rate was used, this difference in activity between fresh and reactivated catalyst was not noticeable.

It is interesting to note the variation of styrene content in the converted products. At the low feed rate, the use of fresh catalyst resulted in a low styrene content (3.7%). Using partially spent catalyst, the styrene content rose considerably (6.6%), while with reactivated catalyst, it was even higher (10.9%). At the faster rate, the same trend was evident, i.e., increased styrene content with the use of reactivated catalyst. For this reason, all further runs were carried out with reactivated catalyst, which seemed to show no decrease in activity even after nine consecutive runs (Run 20).

(2) *Variable Feed Rates at 400° to 650° C.*

Results obtained using variable feed rates at temperatures of 400°, 500°, 600°, and 650° C. are shown in Table II.   In those cases where sufficient gaseous products warranted a gas analysis, the following approximate range of composition was found in the constituents of the gas:—

Constituent	% by volume
Carbon dioxide	6 – 9
Carbon monoxide	14 – 20
Ethylene	2 – 10
Higher unsaturates	Nil
Hydrogen	46 – 63
Saturates	8 – 24

TABLE II

PYROLYSIS OF 1,1-DIPHENYLETHANE OVER MORDEN BENTONITE

Mole ratio of water/diphenylethane = 10/1

Run No.	Temp., °C.	Feed rate*	Vapor products†	Main liquid products, % by wt. of original material					Styrene, % of theoretical yield
				Benzene	Toluene	Ethyl-benzene	Styrene	Total‡	
37	400	0.061	0.75	19.7	—	12.8	5.9	38.4	10.3
17	400	0.122	0.55	12.2	—	7.2	4.9	24.3	8.6
16	500	0.061	1.51	30.2	—	22.0	7.8	60.0	13.7
14	500	0.122	1.04	33.6	—	20.1	11.2	64.9	19.6
15	500	0.244	1.33	30.0	—	12.4	19.1	61.5	33.4
19	500	0.305	0.78	31.4	—	9.7	18.6	59.7	32.6
18	500	0.366	0.73	30.1	—	8.1	19.2	57.4	33.6
21	500	0.488	0.73	27.1	—	6.6	20.1	53.8	35.2
29	550	0.122	10.6	32.7	2.9	13.2	19.0	67.8	33.3
35	550	0.244	8.20	32.0	—	8.9	24.3	65.2	42.5
28	550	0.366	3.64	30.2	—	6.7	24.7	61.6	43.3
36	550	0.488	1.29	27.3	—	5.3	24.6	57.2	43.1
32	600	0.122	14.8	28.7	5.2	10.2	17.2	61.3	30.2
34	600	0.244	8.20	34.9	2.7	9.1	27.6	74.3	48.3
31	600	0.366	7.00	33.4	—	8.5	28.8	70.7	50.5
33	600	0.488	1.82	32.0	—	6.4	29.2	67.6	51.1
39	650	0.549	6.36	35.2	2.3	9.6	26.3	73.4	46.0

* *Moles of diphenylethane per hour per 100 ml. catalyst.*
† *Liters per mole of diphenylethane.*
‡ *Remainder mainly unconverted 1,1-diphenylethane.*

The following conclusions may be drawn from the trends observed:

   (a) Higher temperatures result in increased conversions as well as increased styrene content in the converted products.   The styrene content, however, reaches a maximum at about 600° C.

(*b*) For any given temperature, faster feed rates result in decreased conversions but increased styrene content in the converted products, the styrene content approaching a maximum at rates of about 0.5 mole per hour per 100 ml. catalyst, with a water to oil ratio of 10 to 1. There appears to be an anomalous low conversion obtained at slow feed rates at temperatures of 500° and 600° C.

(*c*) Optimum conditions for styrene production appear to be high temperatures and rapid feed rates. Thus at 600° C. and the fastest rate shown, using a 10 to 1 mole ratio of water as diluent, the 29.2% styrene obtained represents 74.1% of the theoretical yield obtainable at a conversion of 67.6%.

(*d*) At higher temperatures and slower rates, some toluene was obtained; this indicated scission of the ethylbenzene side chain under these severe conditions.

(*e*) Analysis of the gaseous products shows presence of carbon monoxide and dioxide. This could only be due to interaction between the water vapor and free carbon formed during pyrolysis. This question is further elucidated in the following discussion.

(3) *Effect of Water and Nitrogen Diluent on Pyrolysis at 500° C.*

Table III shows the effect of variable water diluent on this pyrolysis. An analysis of the gaseous products from these runs showed the same approximate range of composition as found previously. However, no traces of carbon

TABLE III

EFFECT OF DILUENTS ON PYROLYSIS OF 1,1-DIPHENYLETHANE

Furnace temperature, 500° C.

Run No.	24	27	30	26	41	43
Feed rate, moles per hour per 100 ml. of catalyst						
Diphenylethane	0.366	0.366	0.366	0.366	0.366	0.366
Water	3.72	1.86	0.62	—	—	—
Nitrogen	—	—	—	—	3.72	1.86
Vapor products, liters per mole of diphenylethane	0.85	1.07	1.66	2.42	—	—
Main liquid products, % by wt. of original material						
Benzene	28.5	26.1	22.7	19.3	19.1	21.9
Ethylbenzene	9.4	10.3	12.6	12.9	2.6	5.3
Styrene	18.3	16.1	9.8	4.8	16.5	15.1
* Total	56.2	52.5	45.1	37.0	38.2	42.3
% of theoretical yield of styrene	32.1	28.2	17.2	8.4	28.9	26.5

* *Remainder mainly unconverted diphenylethane.*

monoxide or carbon dioxide could be detected in the gas from Run 26, where no water diluent was used. The importance of the water is easily observed by the marked increase in both the conversion and the proportion of styrene in the converted products, when water vapor is present as a diluent. It can also be noted from the gas analysis data that the presence of carbon monoxide and carbon dioxide is due to the water present, and that there is much more gaseous decomposition in the absence of water diluent. Hence the following conclusions may be drawn:

(a) Presence of water diluent decreases the contact time to such an extent (high molar ratios) that side chain attack is greatly reduced, leading to formation of less gaseous products and less carbonization on the catalyst, and/or

(b) Water vapor prevents the accumulation of carbon on the catalyst by removing it in the form of the two carbon oxides noted.

Either or both of the above explanations would successfully explain the enhanced activity of the catalyst in the presence of water diluent, as shown by the increased conversions obtained. This would also account for the anomalous low conversions obtained at slow rates at 500° and 600° C. It is quite reasonable to assume that at such slow feed rates there would arise increased side chain decomposition with enough carbonization to overcome the effect of the water diluent. This would lead to some deactivation of the catalyst, with consequent low conversion. At 500° C. this effect is apparently noticeable at the slowest feed rate shown, while at 600° C. it is noticeable even at a slightly higher feed rate.

The effect of water diluent on the proportion of styrene in the converted products must also be due to the decreased contact time involved. This agrees with the previously observed effect of feed rate on styrene content, viz.: that decreased contact time leads to increased styrene content.

The results obtained with nitrogen as diluent instead of water are also shown in Table III. The use of such an inert diluent should help to prove whether the water vapor improves the activity of the catalyst by actual removal of carbon, or merely by the prevention of carbonization due to decreased contact time.

It is evident from the results shown that use of nitrogen, at the same vapor dilution ratios as water, did not lead to the same high conversion efficiency. Runs 41 and 43 are comparable, as regards volume dilution ratios, with Runs 24 and 27. Although the use of nitrogen seemed to improve the conversion to a slight extent, it did not approach the effect produced by the use of water vapor. Hence this evidence suggests that the main function of the water diluent lies in the removal of carbon from the catalytic zone. It is interesting to note that the styrene content of the converted products was notably higher when nitrogen was used instead of water. A possible explanation may be that the additional hydrogen produced by the interaction of the water vapor with the carbon might result in some hydrogenation of the styrene to ethylbenzene.

Reaction Mechanism

Any postulated reaction mechanism must account for the following facts:—

(1) Presence of two competitive reactions, one leading to styrene formation, the other to ethylbenzene.

(2) Increase in styrene formation with decrease in contact time either by
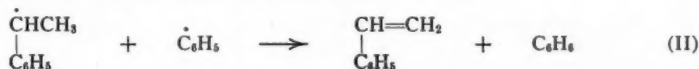   (*a*) Use of diluent such as water or nitrogen, or
   (*b*) Increase in feed rate.

(3) Decrease in styrene formation with the use of a very active catalyst (freshly activated).

The primary decomposition may be postulated as follows:—

$$\underset{\underset{C_6H_5}{|}}{\overset{C_6H_5}{\underset{|}{CHCH_3}}} \longrightarrow \underset{\underset{C_6H_5}{|}}{\overset{\cdot}{CHCH_3}} + \ C_6H_5\cdot \qquad (I)$$
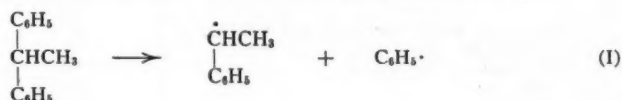
Formation of styrene could then ensue, thus

$$\underset{\underset{C_6H_5}{|}}{\overset{\cdot}{CHCH_3}} + \ \overset{\cdot}{C_6H_5} \longrightarrow \underset{\underset{C_6H_5}{|}}{\overset{CH=CH_2}{}} + \ C_6H_6 \qquad (II)$$

Considerable evidence can be found in the literature for this type of free radical stabilization (2; 9; 11, p. 92). The formation of ethylbenzene, however, would involve a hydrogenation reaction between the styrene and any hydrogen formed from side chain decomposition, thus

$$\underset{\underset{C_6H_5}{|}}{\overset{CH=CH_2}{}} + \ 2H \longrightarrow \underset{\underset{C_6H_5}{|}}{\overset{CH_2CH_3}{}} \qquad (III)$$

although there is the possibility that the ethylbenzene may be formed by a hydrogenation of the free radical shown in (I) above. At higher temperatures (and slow rates), the side reactions become more extensive, and small amounts of toluene are found in the liquid products. This indicates another type of dealkylation reaction, either of the ethylbenzene formed, or of the secondary radical originally formed, thus

$$\underset{\underset{C_6H_5}{|}}{\overset{CH_2CH_3}{}} \longrightarrow \underset{\underset{C_6H_5}{|}}{\overset{\cdot}{CH_2}} + \ \overset{\cdot}{CH_3} \qquad (IV)$$

followed by stabilization of the radicals by means of available hydrogen to form toluene and methane. This type of decomposition of ethylbenzene was found to occur over Morden bentonite at 600° C. by Wasson (15).

The formation of ethylbenzene can be explained by Reaction III. This hydrogenation will depend on the presence of available hydrogen from side chain decomposition. This can be expected to occur whenever the contact time is increased. In order to obtain more evidence as to the possibility of the hydrogenation of styrene to ethylbenzene under these reaction conditions,

several additional runs were carried out, as shown in Table IV. In these runs, an equimolar mixture of styrene and benzene was pyrolyzed at 500° C. and the products analyzed to determine whether any of the styrene had been

TABLE IV

PYROLYSIS OF STYRENE–BENZENE MIXTURE OVER MORDEN BENTONITE

Furnace temperature, 500° C.

Equal feed ratio (gm.) of styrene and benzene

Run No.	44	45
Feed rate, moles per hour per 100 ml. of catalyst		
Styrene	0.178	0.178
Benzene	0.238	0.238
Water	1.24	—
Vapor products, liters per mole of styrene feed	0.51	0.48
Main liquid products, % by wt. of original material		
Benzene	49.3	49.9
Ethylbenzene	10.5	12.8
Styrene	32.4	29.3
* Total	92.2	92.0

* Remainder mainly high boiling residue.

hydrogenated to ethylbenzene. It was hoped that some hydrogen would be available from side chain attack on the original styrene.

The results obtained show that a portion of the styrene has been converted to ethylbenzene. Furthermore, this hydrogenation is slightly more pronounced in the absence of water vapor, just as in the case of diphenylethane. These results show the possibility of the hydrogenation of the styrene formed in the pyrolysis of the diphenylethane. This is the type of hydrogenation postulated by Han-Ying Li (8), who obtained only benzene and ethylbenzene when pyrolyzing 1,1-diphenylethane over acidic white clay at 600° C.

It is reasonable to assume, therefore, that the first stages of pyrolysis of diphenylethane can be explained satisfactorily by Reactions I and II. However, if the contact time is too long, some side chain decomposition also occurs; this results in the formation of hydrogen, converts some of the styrene to ethylbenzene. A diluent, such as water, plays the same role as an increase in feed rate, i.e., it reduced the contact time. This explains the higher proportion of styrene obtained with the use of a water or nitrogen diluent, since the shorter contact time prevents Reaction III.

The behavior of freshly activated catalyst may also be explained by means of this mechanism. The high conversion obtained indicates superior catalyst activity over that of reactivated catalyst. However, this high activity plays

the same role as longer contact time, hence side chain decomposition is encouraged and Reaction III takes place, especially at slower rates. This is corroborated by the fact that the same catalyst, when deactivated by one run, shows a much lower conversion efficiency (Run 12) but produces a much greater proportion of styrene. Further corroboration is supplied by the fact that, at higher feed rates, the activity of freshly activated catalyst does not have nearly the same effect as at slower rates. Thus, at the faster rate, the freshly activated catalyst shows the same conversion efficiency as the reactivated catalyst (Runs 23 and 24), and only a little less styrene formation.

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THE CRITICAL OPALESCENCE OF ETHYLENE[1]

By S. G. Mason[2] and O. Maass

Abstract

The opalescence of ethylene has been investigated under various conditions in the region of the critical temperature. The opalescence of critical fillings increases as the temperature is lowered and passes through a maximum at the critical dispersion temperature T_s. When the system is heated the value depends upon the thermal history, both below and above T_s. Two types of time lag curve are observed in the irreversible region, one in which the opalescence passes through a minimum and then a maximum value, and the other through a minimum only. It is believed on the basis of previous qualitative studies that violent shaking would result in reversibility with respect to changes in temperature. Once the apparent phase discontinuity has disappeared the opalescence becomes reversible as long as condensation is prevented. The opalescence of critical fillings depends upon the density and appears to be a maximum when the two phases are present in equal volumes at T_s. Air and oleic acid present in small quantities depress T_s but do not appear to change the variation of opalescence with $(T - T_s)$ when $T > T_s$. These observations appear to disagree with the classical Einstein–Smoluchowski theory based on light scattering resulting from statistical fluctuations in density. This theory predicts a maximum opalescence at the classical critical temperature, which in the case of ethylene is $0.7°$ C. higher than T_s. If, however, the more recent views of the nature of the $P - V$ isotherms near the critical point are taken into account, some of the conflict disappears.

Introduction

When a sealed tube filled to the critical density is heated, a pronounced turbidity appears in the liquid and vapor phases as the critical temperature is approached, and persists above the temperature of disappearance of the meniscus. Various hypotheses have been advanced to explain this phenomenon. Altschul (1) ascribed the effect to mutual dispersion of the two phases in the critical region. Konowalow (4) concluded that it is caused by transitory condensations upon dust nuclei present. A more satisfactory explanation advanced originally by Küster (5) and subsequently developed quantitatively by Einstein (2), Smoluchowski, and others (16) is based on the scattering of light arising from statistical fluctuations in density. Thus it was shown (2) that to a first approximation the law of scattering is given by the relation.

$$\frac{i}{I} = \frac{\pi^2}{18\mu^4\lambda^4} (\mu^2 - 1)^2(\mu^2 + 2)^2 \cdot \frac{kT}{-v\left(\dfrac{\partial p}{\partial v}\right)_T} \tag{1}$$

In this, I and i are respectively the intensity of incident light and the scattered intensity per unit volume per unit solid angle normal to the incident beam, λ the wave length, μ the average refractive index, k the Boltzmann constant, T the absolute temperature, p the pressure, and v the volume.

When applied to gases at low pressure, this equation accounts satisfactorily for observed scattering phenomena such as the blue of the sky (11).

At the classical critical temperature T_c, where $\left(\frac{\partial p}{\partial v}\right)_T = 0$ and $\left(\frac{\partial^2 p}{\partial v^2}\right)_T = 0$ the compressibility coefficient $-v\left(\frac{\partial p}{\partial v}\right)_T$ is zero and i/I becomes large; above this temperature we can write

$$\left(\frac{\partial p}{\partial v}\right)_T = \left(\frac{\partial^2 p}{\partial v \cdot \partial T}\right)(T - T_c).$$

The scattering coefficient, or opalescence, should therefore be inversely proportional to λ^4 and $(T - T_c)$. This was confirmed approximately by Keesom (3) from measurements on ethylene up to $2.35°$ C. above the critical temperature, which he reported as $11.18°$ C. The latter value is higher than the accepted value of $9.90°$ C. (6) and the difference was attributed to impurities. Schröer (14, 15), from purely qualitative observations, concluded that impurities enhance the opalescence. Ramanathan (12) found the opalescence of liquid and gaseous ether to be in accord with Equation (1) except in the region of the critical point.

The present investigation was undertaken in an attempt to confirm and extend a number of qualitative observations that had been made of the effect of temperature and thermal history in stationary and shaken bombs of ethane and ethylene near the temperature of disappearance of the meniscus (7, 10). It was, for example noticed that the point of maximum opalescence in vigorously shaken bombs occurred at the critical dispersion temperature T_s, which is appreciably lower than the classical critical temperature T_c. On heating a stationary bomb, the opalescence was not uniformly distributed through either the liquid or vapor phases but was concentrated in the vicinity of the meniscus and was dependent upon the previous thermal history of the system, exhibiting hysteresis phenomena in the same manner as other physical properties.

The present investigation was of an exploratory nature and an experimental technique was evolved to examine aspects that could not be covered in the investigations of Keesom and Ramanathan. It should be emphasized from the outset that the data obtained are not suitable for quantitative evaluation of the variation of the scattering coefficient except in the immediate neighborhood of the critical temperature In order that these limitations may be clearly understood the method used is given in some detail.

Experimental Part

The experimental arrangement for measuring the opalescence is shown schematically in Fig. 1. A flat-bottom bomb A was constructed from Pyrex glass 10 mm. inside diameter and 2 mm. wall thickness. The volume was 3 cc. This bomb, containing ethylene, fitted snugly into a thin-walled glass tube B, which, in turn, rested upon the glass face of a Weston Photronic Cell C. The light source was a 10 v. 75 w. illumination lamp D, placed 2 in. from

the tube. The light that passed through the rectangular apertures E and F into the bomb was scattered upon the partially exposed surface of the photocell; that which passed through the aperture G impinged upon the photronic cell H to give a measure of source intensity.
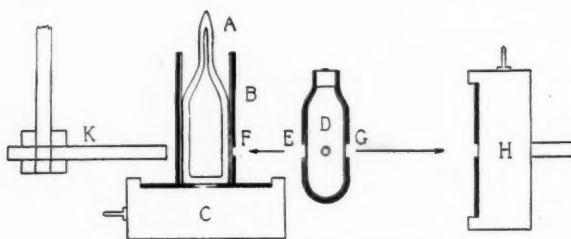

FIG. 1.   *Experimental arrangement.*

The rectangular aperture F was 6 by 10 mm.; the long edge was perpendicular to the axis and 17 mm. from the bottom of B. The exposed surface of cell C was 9 mm. in diameter and that of cell H 6 mm. in diameter. Unexposed surfaces were covered with optical black paint. The system was mounted on a frame of sheet aluminum. This frame was rigidly supported in a water thermostat bath whose temperature could be manually controlled to $\pm 0.0005°$ C. Temperatures were measured to a differential accuracy of $0.001°$ C. with a Beckmann thermometer and an absolute accuracy of $0.01°$ C. with a standard Reichanstalt thermometer.

The intensity of scattered light was measured by means of a damped, low resistance (50 ohms), calibrated d'Arsonval galvanometer having a sensitivity of 0.8 mm. per μv. Cell H was connected to a 10.0 ohm millivoltmeter shunted with 4.0 ohms.

The lamp D was supplied from a 110/10 v. 60 cycle transformer. The variation in the output, as recorded by cell H, was small and very gradual.

The optical system was rather crude: polychromatic light was used, a correction for reflection from the walls of the cell and containing tube was necessary, and the results did not readily lend themselves to the calculation of scattering coefficients. However, it was adequate for this preliminary investigation. The method was sensitive, photocell fatigue effects were negligible, and the runs were readily reproducible.

Ethylene was chosen because of its convenient critical constants. It was purified by distillation of 99.9% pure material in a Podbelniak column and was condensed into one of the two bombs used from a calibrated storage system to a critical filling density. In most cases the density was later determined more accurately by weighing.

In a typical run, the light source was turned on at least two hours before any measurements were made, in order to bring the photocell H to equilibrium. The bomb was then placed in position and the bath raised to $16°$ C. to destroy

any residual heterogeneity.   Above this temperature the response of the photo-
cell was constant, and the opalescence was taken to be zero.   The galvan-
ometer reading at this temperature was taken as the zero correction resulting
from spurious scattering from the walls of the various parts of the system.

Simultaneous readings of temperature, galvanometer, and millivoltmeter
were recorded.   At least six minutes was allowed for the cell to come to thermal
equilibrium with the bath, although no differences in opalescence could be
detected after two minutes at a given temperature on cooling cycles.   On
certain portions of the heating cycle the time lags were considerably greater
and of a different nature.

The degree of opalescence is expressed arbitrarily as the galvanometer
deflection after applying corrections for nonlinearity of the meter and scale,
changes in source intensity, and the corrected zero opalescence reading at
16° C.   Since all the readings of the source intensity were within 3% of the
mean value of 1.400 mv. this was taken as the standard intensity.   The zero
correction amounted to about 2 cm.

Results

A. Influence of Temperature and Thermal History

In Fig. 2 are plotted the results of a run on ethylene in bomb No. 1 filled
to a calculated density of 0.215 gm. per cc.   The critical dispersion tem-
perature T_s was found to be $9.20 \pm 0.01°$ C.   All subsequent critical fillings
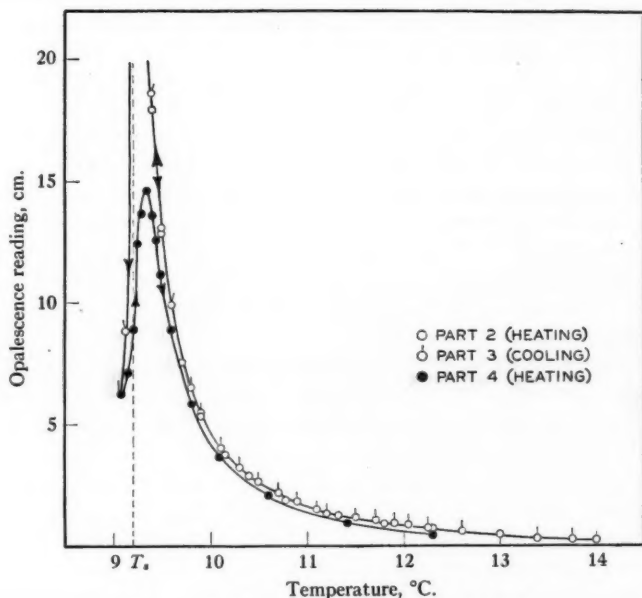

FIG. 2.   Influence of thermal history on the opalescence.

of pure ethylene had the same T_s on the Beckmann thermometer. The thermal history of the system in the course of the opalescence measurements was as follows:—

1. The bomb was heated to 16° C. to destroy any discontinuity and then cooled to 9.345° C.

2. Readings of opalescence were made at increasing temperatures from 9.345° C. to 16° C.

3. Part 2 was reversed and the system cooled through the point of reappearance of the meniscus (9.200° C.) to 9.075° C.

4. Readings were made at increasing temperatures from 9.075° C. to 12.3° C.

All opalescence readings were made at 7-minute intervals and are equilibrium values except for those in Part 4, where, as later became apparent, insufficient time was allowed.

This series shows, as was repeatedly confirmed in other experiments at various densities, that the opalescence is not only reversible with respect to changes in temperature as long as condensation is prevented but also rises to a sharp maximum at the critical dispersion temperature rather than the classical critical temperature of 9.90° C. as predicted by Equation (1). Once condensation has occurred, however, the opalescence is no longer reversible, and the hysteresis shown in many other physical properties is exhibited.

A number of experiments were carried out to determine the nature of the nonequilibrium portion of the curve, i.e., corresponding to Part 4 above. It was found that its shape depends upon the rate of heating and the lowest temperature in the cycle. It was observed that the greater the rate of heating the less the opalescence at a given temperature and the higher the temperature of maximum opalescence. The lower the minimum temperature of the cycle the less was the opalescence at a given temperature and a fixed rate of heating.

In one series of runs attempts were made to allow the system to come to an equilibrium at each temperature. These measurements were carried out at a calculated density of 0.203 gm. per cc. using bomb No. 2. Starting at 5.10° C., opalescence readings were taken at increasing temperatures up to 16.20° C. and then at decreasing temperatures to 9.200° C. just before condensation occurred.

Between 5.10° C. and 8.5° C. the opalescence became constant within two minutes. Between 8.5° C. and 9.185° C. the time to equilibrium rose rapidly, and exceeded three hours at the latter temperature. Above 9.285° C. the time fell rapidly from 40 to 2 min.

The time lags encountered between 8.5° C. and 9.185° C. were unusual in that the opalescence went through a minimum and then a maximum. The effect is shown in Fig. 3 where values at 9.185° C. are plotted, and the opalescence taken at zero time is taken as the last value at the preceding temperature which for the case illustrated was 9.085° C. The same behavior was observed in two other runs.

Above 9.200° C. on the heating portion, the opalescence passed through a minimum and then rose asymptotically to a maximum.   Fig. 3 includes the data at 9.285° C.
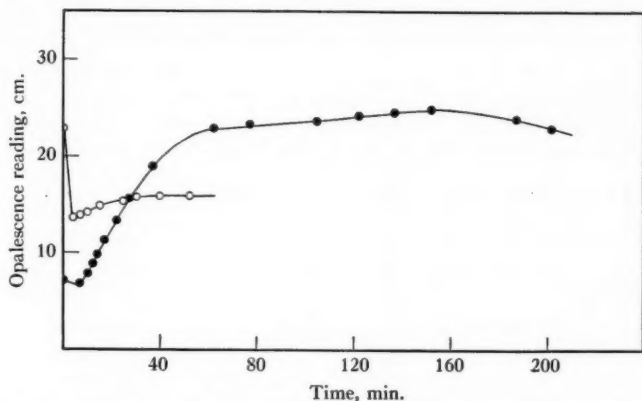

. FIG. 3.   *Time lags observed on heating.* ● *Temperature, 9.185° C.*   ○ *Temperature, 9.285° C.*

The 'equilibrium' values are given in Table I and are plotted in Fig. 4.   In the range between 8.5° C. and 9.185° C. the readings are the maxima observed. For purposes of comparison the times corresponding to the maximum opalescence readings are included in the table.

TABLE I

OPALESCENCE READINGS—BOMB NO. 2—DENSITY 0.203 GM. PER CC.

Temp., °C.	Opalescence, cm.	Time, min.	Temp., °C.	Opalescence, cm.	Time, min.
Part 1—Heating portion			Part 2—Cooling portion		
5.10	1.37	6	14.00	0.26	6
5.80	1.49	6	13.20	0.33	6
6.40	1.24	6	12.08	0.62	6
7.00	1.15	6	11.36	0.94	6
7.60	1.07	6	10.58	1.90	6
8.18	1.21	6	10.18	2.82	6
8.48	1.47	12	9.785	5.06	6
8.68	1.89	15	9.635	6.66	6
8.88	3.00	20	9.485	9.53	6
9.085	7.37	32	9.392	12.41	6
9.185	24.90	152	9.285	18.69	6
9.285	15.88	40	9.234	23.56	6
9.535	7.67	13	9.205	26.78	6
9.785	4.83	10	9.200	37.1	6
10.28	2.54	8			
12.28	0.59	7			
14.00	0.22	7			
16.20	0.00	6			

As in the cycle shown in Fig. 2, a 'discontinuity' in opalescence is exhibited, although its magnitude is considerably reduced, and the maxima appear to occur at the same temperature on the heating and cooling portions. The shape of the reversible portion is the same for both series, but there are variations due to different bomb dimensions and, as will be seen below, different filling densities.

It will be noted that the curve in Fig. 4 passes through a minimum at 7.5° C. Below 9.185° C. there is a sharply defined meniscus which would reflect on the photocell a certain amount of light depending upon the difference of
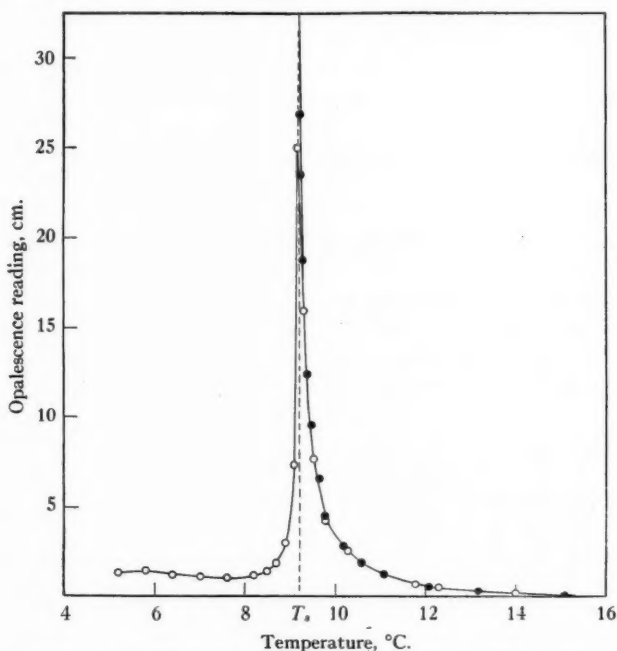

FIG. 4. *'Equilibrium' values of opalescence.* ● *Heating.* ○ *Cooling.*

refractive index across the interface. As the temperature increases, the difference diminishes and with it the contribution of reflected light. One would therefore expect the opalescence reading, consisting of true opalescence plus the reflection at the meniscus, to pass through a minimum value.

The reciprocal opalescence in the reversible region above T_s is plotted against $(T - T_s)$ in Fig. 5 from the data of Table I. Values calculated from Keesom's data (3) are included for comparison. Because of the relative degrees of precision in the opalescence and temperature measurements, this method of plotting the data is less suitable in the present instance than the inverse method used in Fig. 6, but gives less scatter in the case of Keesom's

values where temperatures were measured only to $0.01°$ C. The adjustment of Keesom's arbitrary opalescence scale to the arbitrary scale of Fig. 5 was carried out as follows. T_s was taken to be $11.18°$ C., the reported critical
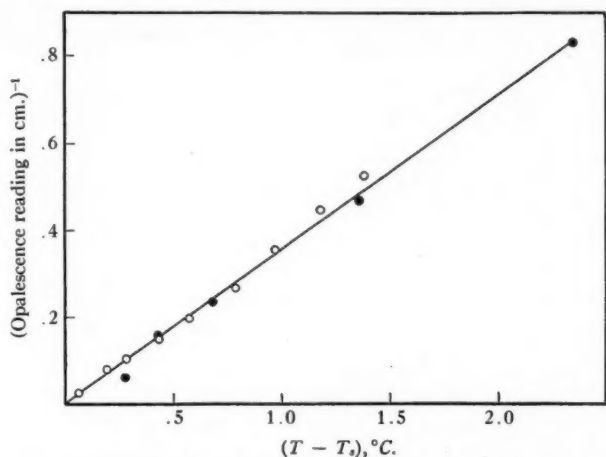

FIG. 5. *Comparison of present data with Keesom's (3).* ○ *Present data (Table I); T_s = 9.20° C.* ● *Keesom's data to same scale; T_s taken as 11.18° C.*

temperature of the sample. The opalescence at $11.86°$ C., or at $T - T_s = 0.68°$ C., was assumed to be the same as that determined from an interpolation of the data of Table I at $9.88°$ C., thus providing a conversion factor for bringing the two sets of data into alignment. It will be observed that the reciprocal of Keesom's opalescence varies linearly with the temperature and extrapolates to zero at $11.18°$ C. The data of the present investigation agree fairly well at low values of $(T - T_s)$. Keesom does not state how the critical temperature of his sample was determined, although it would appear from the present data that T_s rather than T_c was reported.

B. Influence of Average Density

Three separate runs in the reversible region were made in bomb No. 2 at three different critical filling densities. Typical results are shown in Table II for densities of 0.2140, 0.2127, and 0.203 gm. per cc. Unfortunately before the last stated density could be determined gravimetrically, the capillary burst, and the value given (accurate to 0.5%) was determined when condensing the ethylene in from the filling system.

It is evident that the opalescence of the critical fillings is dependent upon the average density as well as the temperature, and for the densities examined appears to be greatest at 0.2127.

It was found that on shaking, the meniscus in the 0.2127 filling disappeared at the center of the bomb. This density corresponds to the mid-point of coexistence curve of ethylene at the critical dispersion temperature (10). The

meniscus of the 0.2140 filling disappeared slightly above the center and that of the 0.203 filling near the bottom of the bomb. One may tentatively conclude, therefore, that maximum opalescence occurs at a density corresponding to equal volumes of liquid and vapor at T_s.

TABLE II

INFLUENCE OF AVERAGE DENSITY

Temperature, °C.	Opalescence, cm.		
	0.203 gm./cc.	0.2127 gm./cc.	0.2140 gm./cc.
9.200	37.1	60.1	54.0
9.205	26.8	56.9	—
9.211	—	—	47.4
9.214	—	51.2	—
9.232	—	—	40.6
9.234	23.6	43.4	—
9.265	—	35.4	32.4
9.285	18.7	—	28.7
9.885	—	5.2	—
9.903	—	—	4.8
9.985	3.7	4.5	—

C. Effect of Impurities

As pointed out in the Introduction, some doubt exists with regard to the influence of impurities. It was therefore decided to examine the effect of air and oleic acid, which were considered to represent extremes in influencing critical temperature phenomena.

Bomb No. 1 filled to a density of 0.215 gm. per cc. (see Section A above) was immersed in liquid air until the ethylene was frozen solid. The tip was then broken, air admitted at atmospheric pressure and the bomb resealed to the same volume. The air content was about 1% of the ethylene.

On examining the filling, it was found that while no change occurred in the position of disappearance of the meniscus, T_s was lowered to 8.475° C.

The opalescence of ethylene and ethylene–air in the reversible region is plotted against $(T - T_s)^{-1}$ in Fig. 6, which for reasons of relative sensitivity is a more adequate method of plotting the data than that in Fig. 5.

The effect of oleic acid was examined in bomb No. 2 to which a minute droplet was added through a fine capillary. The bomb was then filled with pure ethylene to a density of 0.2045 gm. per cc. This was found to be a critical filling with a depression of T_s to 9.150° C. Only a small quantity (estimated to be less than 0.1% based on ethylene) of the oleic acid dissolved.

The opalescence reading vs. $(T - T_s)^{-1}$ is also shown in Fig. 6. Comparative data for pure ethylene in bomb No. 2 at the 0.203 gm. per cc. filling are included. The pronounced difference in position of the two curves is due

to the fact that different bombs were used; the displacement is therefore mainly due to differences in geometry and hence in the scale of the absolute scattering coefficient and should be so interpreted.
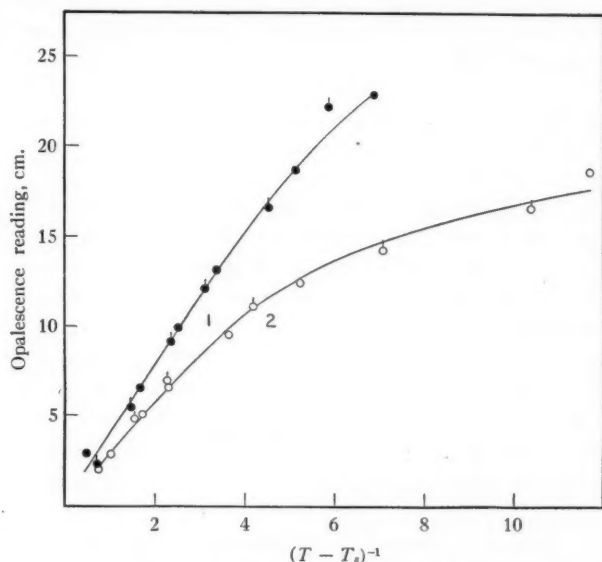

FIG. 6. *Effect of impurities. Curve 1. Ethylene and ethylene plus air (crossed circles). Bomb No. 1. Curve 2. Ethylene and ethylene plus oleic acid (crossed circles). Bomb No. 2.*

It is apparent from these results that with both air and oleic acid (taking into account the difference in densities in the second case) the change in opalescence with $(T - T_s)$ is not affected by the presence of impurities except where T approaches T_s. In this region air enhances the opalescence while oleic acid reduces it. A slight trend is detectable in the upper portion of the curves in Fig. 6. The effect becomes more pronounced as $(T - T_s)$ is reduced but is not shown in the figure because of scale considerations. At T_s, for example, the addition of air changed the opalescence by a factor of 1.5 and of oleic acid by a factor of 0.6 of the corresponding values for the pure systems.

Discussion

These results are in agreement with the qualitative observations made in a previous investigation of ethylene and ethane (7, 10). The opalescence of all critical fillings increases as the temperature is lowered, passing through a maximum at T_s, and subsequently decreasing. It is not reversible with respect to temperature, once condensation has occurred, within the considerable times allowed in these experiments for the establishment of equilibrium. It is believed however that violent shaking would result in reversibility (7).

Once the apparent discontinuity has disappeared the opalescence becomes reversible. The opalescence of critical fillings depends upon the density and appears to be a maximum when the two phases are present in roughly equal volumes at T_s. Such a conclusion must, however, be regarded as purely tentative. Impurities, while influencing T_s, do not appear to affect the variation of opalescence with $(T - T_s)$ for $T > T_s$ once reversibility has been established.

These observations do not agree with the values predicted on the basis of Equation (1). It is acknowledged that the slight aberration from the linear dependence of the reciprocal opalescence upon temperature confirmed by Keesom may be due to the limitations of the experimental method used here, where secondary scattering can introduce errors. The principal point of disagreement is the temperature of maximum opalescence, which occurs at T_s rather than T_c. In the case of ethylene these temperatures are 9.20° C. and 9.90° C. respectively.

The findings are not, however, in basic conflict with the original views of Einstein and Smoluchowski (2, 16), if the nature of the $P - V$ isotherms and the properties of the anomalous two phase system in the region of the critical temperature are taken into account. Detailed development of this idea is reserved for a future publication but brief mention of it can be made at this stage.

It has been established experimentally for ethylene in this laboratory (6, 10) and predicted independently for all substances by Mayer and Harrison (8, 9) from a statistical mechanical treatment of condensation, that below the classical critical temperature T_c and above the critical dispersion temperature T_s (termed T_m by Mayer) there is a finite area on the $P - V$ plane corresponding to an anomalous homogeneous phase in which $\left(\dfrac{\partial p}{\partial v}\right)_T$, $\left(\dfrac{\partial^2 p}{\partial v^2}\right)_T$ etc. $= 0$. The demarcation of this area by Maass $et\ al.$ (6) from their experimental data has been questioned recently by Rice (13), but if the existence of such an area is accepted, it follows that the mean square fluctuation in density, and hence the opalescence, will be a maximum at the temperature at which $\left(\dfrac{\partial p}{\partial v}\right)_T = 0$ over the maximum range of densities. This temperature is T_s.

It remains to make brief reference to the time lags observed (Fig. 3). The maximum opalescence at 9.18° C. can be explained as follows. In heating the stationary bomb from below T_s, the opalescence first appears in the region of the meniscus opposite the aperture F (Fig. 1), and subsequently expands through both phases (7). Since light scattered from the point of entry can be attenuated by secondary scattering before reaching the photocell, clearly the opalescence measured by the photocell output can pass through a maximum. Such time lags are therefore not believed to be of fundamental significance.

The minimum, on the other hand, occurs immediately after increasing the temperature both above and below T, on the heating cycle and cannot be due to a similar mechanism. No adequate explanation can be advanced for this phenomenon. It is our belief however that it is of fundamental importance and should be investigated further.

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NOTES

The Structure of Boron Hydrides[1]

These compounds are of much interest at the moment, and an advance note on the forms suggested by a modified valence theory might therefore be useful.

The whole of this theory and its consequences are too voluminous to discuss here in detail, but it is hoped to publish fully in the near future. It is adequate at the moment to note that when B uses tetrahedral orientation of its three valence fields, the fourth tetrahedral direction is assumed to be occupied by a resultant field of exactly the same nature as a normal valence field, but reversed in sign (although no orbital electron is occupied directly in producing this field), and it is further considered that H has an exactly similar field in the direction away from its B bond. It is also suggested, especially in such cases as the present when only weak B–H bonds form, that the above residual fields are of a magnitude approximately equal to the strength of the B–H bond itself, and consequently these reversed residual fields constitute a 'reversed valence', of a nature similar to the normal valence, but which can be used only between atom pairs both of which have such a reversed field. These 'reversed valencies' are marked + in structural formulae to distinguish them from the normal type for which a bar, or − sign is used.

General consideration of the effects noted in many compounds also suggests that in the H atom, this reversed valence field may be available at a direction of either 180° or 90° to the B–H bond, or at slight strain from these directions.

B_2H_6. This molecule is then considered as resulting from the + polymerization of two BH_3 groups:
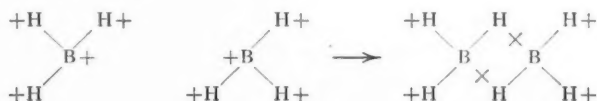
Since such polymerization eliminates four of the eight reversed fields, it is presumed that this therefore produces a molecule of lower energy than direct B + B bonding. Since this molecule in fact appears to be of 'bridge' form it might therefore be anticipated that when the energetics of the case are available they should substantiate the B–H ring polymerization. In writing this formula the residual fields on the terminal H atoms are disregarded, although these are presumably responsible for the great reactivity of diborane.

It will be seen that this is the structure first suggested by Dilthey (3), and later found by Dyatkina and Syrkin by X-ray methods (4), although they could offer no suggestion concerning the source of the unusual bonds.

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In the present models it is suggested that the basis is very simple; if H forms a weak bond, such as it does with B, the remainder of its orbital field is available on the other side of the H atom as a reversed valence. These four 'half-bonds' therefore join the boron atoms with the equivalent of a full valence, and the structure is possible because both B and H have similar reversed fields. It is further suggested that there is no resonance exchange of the '± bridge' bonds, otherwise the molecule would be more stable and the H acidic, these bonds however are considered as thermally labile, and therefore effectively equivalent.

All the boron hydrides will be discussed later, but two others are of present interest.

B_5H_9. This molecule is considered as of pentagon shape, and with careful adjustment of the spacings a form can be obtained, Fig. 1, which appears to fill all the requirements shown by Silbiger and Bauer (8) by electron diffraction methods.
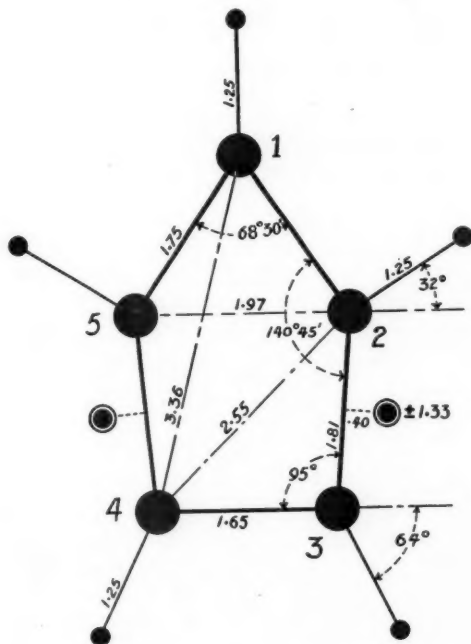

FIG. 1. *Suggested structure of* B_5H_9.

It will be seen that this closely resembles the form suggested by Pitzer (7), but it is assumed that the B atoms using the 'H ± bridge' structure can approach in their other valence to 1.65 Å, or rather more closely than is previously suggested for covalent B bonds, while similar unbonded B atoms are in this

model only 1.97 Å apart. This form is suggested since all spacings in this structure agree very closely with the required limits, and such agreement cannot be obtained by other adjustment of a pentagon.

$B_{10}H_{14}$. In these models this molecule, Fig. 2, is obtained from B_5H_9 by dimerization, and subsequent transfer of the '± bridge' H atoms to adjacent B atoms (since one end of each such bridge would otherwise have no H). In
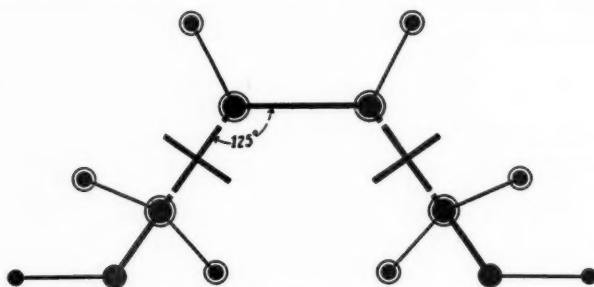
FIG. 2.   *Suggested $B_{10}H_{14}$ molecule.   Edge view.   Double circles are two atoms in line.*

this molecule therefore no bridge structure is present, but the + B bond discussed above, when used between suitable atoms, is used exactly as if it were a normal bond and is not thermally labile at room temperature. It
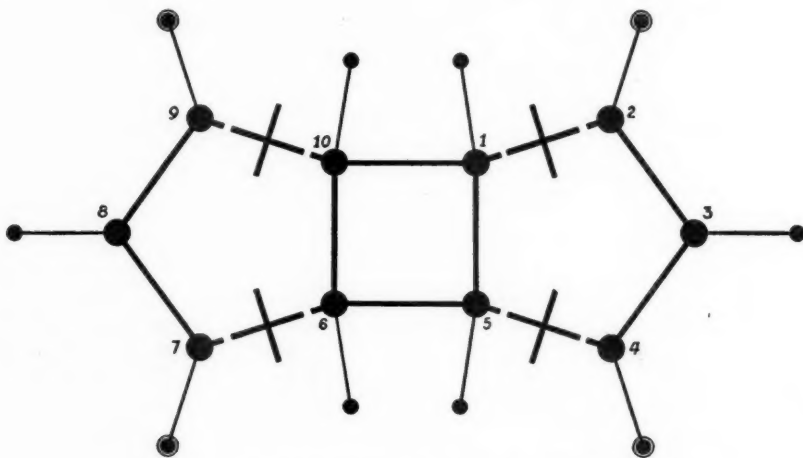
FIG. 2A.   *Suggested structure of $B_{10}H_{14}$ (molecule flattened out).*

might be considered that the B_4 ring might be severely strained, but B bond angles have hardly half the stiffness of C bonds (1 and 2) and the strain is probably of little consequence.

With tetrahedral bond angles where possible, the planes of the B_5 and B_4 rings should form angles of 121°, but while the R.D. pattern would then fit the data of Silbiger and Bauer (8) for the shorter spacings, it is slightly too short throughout the longer spacings. It is assumed therefore that the molecular distribution and strain in the B_4 ring cause the interplanar angles to be increased slightly, and it is found that at 125° an excellent match is provided for all details in the R.D. curve, using B–B spacing of 1.76 Å, and B–H spacing of 1.28 Å.

A molecule of this form should appear in *cis*- and *trans*-forms, but it is assumed that the *cis*-form predominates since the *trans*-form does not fit the E.D. data quite as well. The terminal H atoms have also been drawn as at tetrahedral angles, but since the terminal B atoms may possibly revert to coplanar bonds experiment only could settle this point.

Data from X-ray diffraction methods, giving a 'clamshell' form for $B_{10}H_{14}$, have recently been presented by Kasper, Lucht, and Harker (5, 6) but unfortunately this form gives many B–B spacings from 3.1 to 3.4 Å, while the R.D. graph of (8) shows a deep valley throughout this range. It might be noted that the dimensions giving this difficulty (B2 − 4″; 2 − 2′; 3 − 3′; 4 − 4″) are all in the long direction, taken through the symmetry plane. It would appear, therefore, that while the 'clamshell' form may be correct in many respects, the length may need readjustment in some manner.

The 5.4.5 ring model discussed above was made before electron or X-ray diffraction data were available, but it will be seen that in effect it combines the planes and angles shown by X-rays with the general form selected by E.D. methods, but uses two bonds between the end rings, and therefore avoids complexities due to rotation. It will also be seen from the table that the *cis*-form fits the R.D. requirements very closely.

B–B SPACINGS IN $B_{10}H_{14}$ (FIG. 2)

| Type of spacing	Number	*Cis*, Å	*Trans*, Å
B–B, 1 − 2	12	1.76	1.76
B–B–B, 1 − 3	10	2.84	2.84
1 − 6	2	2.49	2.49
1 − 7	4	3.81	3.81
1 − 8	4	4.08	4.08
1 − 9	4	3.09	3.09
2 − 7	2	4.64	5.39
2 − 9	2	3.68	4.58
2 − 8	4	4.58	5.75
3 − 8	1	4.86	6.57

(B–H and H–H spacings add but little to the character of these data.)

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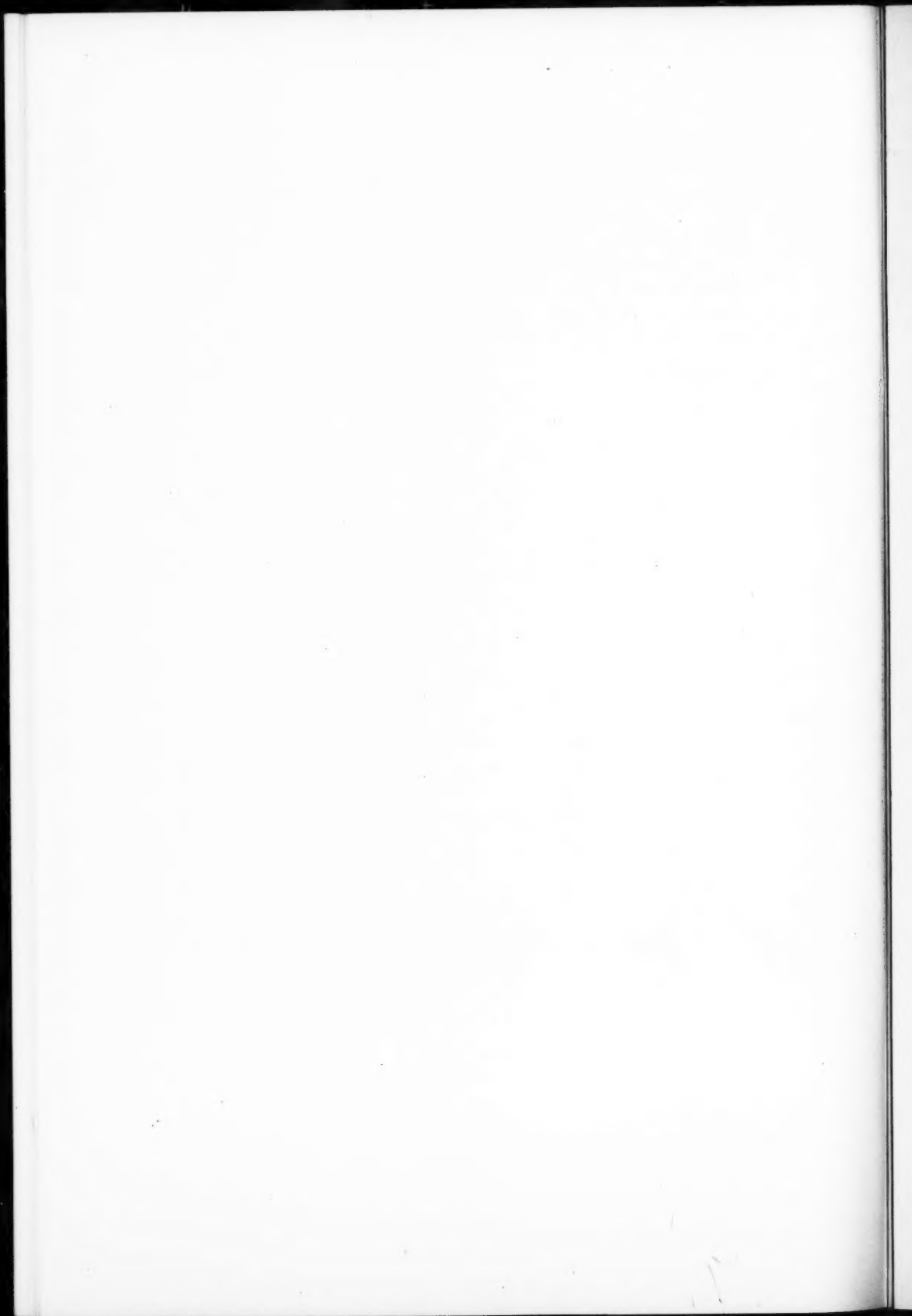
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